INVESTIGATION OF LABORATORY ASPHALT AGING PROCESSES FOR DEVELOPMENT OF AN EFFECTIVE PROCEDURE TO CHARACTERIZE ASPHALT DURABILITY

By

CHUI-TE CHIU

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1994

Dedicated to my parents, sisters, brothers, and wife
for their love and support.

ACKNOWLEDGEMENTS

The author wishes to express immeasurable appreciation to his advisor and supervisory committee chair, Dr. Mang Tia, for his patience and advice throughout his graduate school career. Without his support and guidance this work would not have been possible.

Special thanks go to Dr. Byron E. Ruth, who has kindly served as the cochairman of his supervisory committee, for his advice and encouragement throughout the challenging stages of this study. Sincere thanks are given to the rest of his supervisory committee, Dr. David Bloomquist, Dr. Andre I. Khuri, and Mr. Gale C. Page, from whom he has benefitted tremendously.

Thanks are also extended to the Florida Department of Transportation (FDOT) for providing the financial support and to the FDOT Materials Office personnel, particularly Mr. Kenneth H. Murphy, Randy C. West, Edward Leitner, Toby Dillow, Glen Schiller, and Aaron Turner, for their help and for kindly sharing their experience.

The author would like to thank the University of Florida and the Department of Civil Engineering faculty, staff, and students for making his educational experience here so meaningful and rewarding both academically and socially. His thanks also go to Mr. Danny Richardson, engineer of the structural and materials laboratory, for his assistance in maintaining the testing equipment. The graduate students in the hardworking materials

group, particularly Shin-Che Huang, Patrick B. Upshaw, Chuang-Tsair Shih, Tim Wattleworth, Ming-Gin Lee, and Bob Casper, will always be remembered for their help and exchange of knowledge through brainstorming discussions.

Finally, the author is deeply indebted to his family and his wife, Win-Jane, for their love, encouragement, and understanding throughout his studies.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

INVESTIGATION OF LABORATORY ASPHALT AGING PROCESSES FOR DEVELOPMENT OF AN EFFECTIVE PROCEDURE TO CHARACTERIZE ASPHALT DURABILITY

By

Chui-Te Chiu

April 1994

Chairman: Mang Tia
Cochairman: Byron E. Ruth
Major Department: Civil Engineering

This study investigated a variety of laboratory aging processes on asphalt binders and asphalt mixtures, which were used for simulating the long-term aging of asphalt binders in service. The binder-aging methods investigated include (1) an extended TFOT, (2) a UV chamber, (3) the California Tilt Oven (CTO), and (4) the Pressure Aging Vessel (PAV) on asphalt binders. Different laboratory mixture-aging procedures examined include (1) a forced-draft oven at 60 °C for 28 days, (2) a UV chamber at 60 °C for 28 days, (3) the SHRP (Strategic Highway Research Program) proposed short-term oven aging (STOA),

and (4) the SHRP proposed long-term oven aging (LTOA). Marshall specimens aged under natural sunlight up to four years and core samples from actual paving projects in Florida were also evaluated to correlate the effects of laboratory aging to those of actual aging under Florida conditions. The tests that were used to evaluate the aged binders and recovered binders include penetration, absolute viscosity, Schweyer rheometer, and infrared absorption spectral analysis.

The results show that an asphalt could age differently in different aging processes while different asphalts could age differently in the same environment. The ranking of aging severity among different asphalts could be different by using different evaluation parameters. Due to the insensitivity of consistency measurements at lower temperatures, the most sensitive parameter for characterizing the aging severity of asphalt binders was found to be the aging index at 60 °C, which is the ratio of absolute viscosities at 60 °C of the aged residue to that of the original asphalt. Asphalts from different sources exhibit differentiable degrees of volatile loss when subjected to TFOT at higher temperature. The UV light in the UV chamber was found to be effective only in aging the surfaces of the binder samples. Low viscosity asphalts were found to age more in the CTO process. The aging effect of natural exposure for four years on compacted Marshall samples can be simulated in the laboratory by using the PAV at 110 °C for 20 hours. This PAV process is suggested to simulate the long-term aging of asphalt binders in Florida. For conventional asphalts, a viscosity value of 90,000 poises at 60 °C is a suggested limit for prevention of thermal cracking.

CHAPTER 1
INTRODUCTION

1.1 Background

A pavement engineer is more concerned with the properties of an aged asphalt than those of the original asphalt. As long as the asphalt can be pumped, sprayed and mixed properly with aggregate, the original properties of the asphalt should be of less interest to us. Due to the fact that current specifications focus more on the properties of original asphalt, it has been the experience of highway agencies that, at times, an asphalt may meet current specifications and yet show a poor long-term performance.

As an asphalt ages with time, it becomes harder and may be too brittle to sustain thermal strains induced by high temperature differential in the pavement structure. This problem has been made more critical in recent years by the following three factors [1]:

(1) Asphalts of higher viscosity have often been used to produce asphalt mixtures of higher stability at high temperature (such as at 60 °C) in order to minimize shoving and rutting due to increased vehicle weights and tire pressures. However, using a high-viscosity binder would make the asphalt mixture more susceptible to low-temperature cracking and the effect of further hardening of the binder more detrimental.

(2) There has been increased usage of modified asphalts to attempt to produce asphalt mixtures of improved strength and reduced temperature

susceptibility. However, there are uncertainties about the durability of these modified asphalts.

(3) The new refinery processes, which oil producers have adopted in recent years to extract more light weight fractions from crude oil, may have produced asphalts with different chemical compositions and aging characteristics compared with asphalts produced in the past.

A knowledge of the properties of an aged asphalt (either conventional or modified) and its rate of age hardening is important in the prediction of the long-term performance of an asphalt mixture. The aging characteristics of the asphalt cement should be included in the specifications in order to ensure the durability of a pavement. A possible approach to this problem is to subject the asphalt to an accelerated aging process, which simulates the effects of aging under actual service conditions and to measure the changes in the asphalt properties. These measurements, when correlated to the field performance, could be used for the selection of durable asphalts. Thus, the simulation of age hardening of asphalts has been a major topic of durability studies in the past 50 years.

The TFOT and RTFOT tests have served to screen out asphalts that showed excessive change in physical properties when subjected to the hot mixing process. Although the tests predict the properties of asphalt at the time of construction, they do not provide adequate information on changes in asphalt properties during service. It is possible that an asphalt that is not durable could perform well in the TFOT or RTFOT tests.

A variety of methods have been investigated and proposed to simulate the aging of asphalt during field service. No satisfactory test for estimating field hardening has been accepted for use. Recent studies at the University of Florida found that it is possible to simulate the effects of aging during service as well as that of the hot mixing process by using the TFOT or RTFOT at higher temperatures. The use of an ultraviolet (UV) oven has been developed to simulate the effects of heat, UV light, and air on asphalt mixtures. A pressure aging vessel using a relatively lower process temperature has been proposed by SHRP to simulate long-term asphalt aging. The argument for the use of a lower process temperature is that it is more representative of the temperature of the pavement in service. These proposed methods need to be evaluated and compared with one another before being introduced into the asphalt specifications.

1.2 Study Objectives

Reasonable artificial aging processes and reliable measurements are involved in the prediction of asphalt aging. This research involves performing various promising aging simulation methods on asphalt binders and asphalt mixtures. The aging methods on binders include the modified TFOT, California Tilt Oven, Ultraviolet chamber, and Pressure Aging Vessel processes. The methods of age hardening of asphalt mixtures include subjecting loose mixtures and compacted Marshall samples to a UV chamber and a forced-draft oven and exposing Marshall samples to natural sunlight. These test results were correlated to those of core samples from actual paving projects to determine their applicability to Florida service conditions. Penetration, absolute viscosity, low temperature viscosity, and IR absorption spectra are used as the evaluation parameters.

The main objectives of this study are as follows:

(1) To compare the aging effects (on asphalts) of the TFOT at 140, 163, and 185 °C (285, 325, and 365 °F) to those of the UV chamber, the California Tilt Oven, the Pressure Aging Vessel, and the modified TFOT using 25 g. samples and to determine their relationships.

(2) To determine the relationship between the asphalt aging under various artificial processes and natural aging of asphalt mixtures under typical Florida conditions.

(3) To determine the appropriate artificial aging procedures to be used in the evaluation of asphalt binders and asphalt mixtures for long-term durability in Florida.

1.3 Scope of Study

This study is mainly a laboratory investigation to evaluate a variety of aging processes used for simulating the long-term aging of asphalt binders. Four promising methods investigated in this study include (1) an extended TFOT, (2) a UV chamber, (3) the California Tilt Oven (CTO), and (4) the Pressure Aging Vessel (PAV). A few conventional asphalts commonly used in Florida and a few modified binders were subjected to these aging processes, and their aged residues were tested for comparison of aging severity.

In order to correlate binder hardening to mixture hardening, a few aging processes were performed on loose mixtures that were fabricated in the laboratory by blending one type of aggregate and gradation with the same conventional asphalts used in the binder

study. An extraction and recovery procedure was then performed on the aged loose mixtures. The properties of the recovered binders were measured and compared with those of the aged residues of different binder aging methods. Test results collected from a few paving projects were used to correlate the laboratory aging to the field aging under Florida conditions.

Penetration test at 25 °C, viscosity tests at 60, 25, and 5 °C, and an infrared absorption spectral analysis were used to measure the changes of binder properties. However, the new SHRP binder tests were not performed since the test equipment was not available at the time of this study.

CHAPTER 2
LITERATURE REVIEW

2.1 Pavement Failure Caused by Aging

Through an evaluation of full-scale pavement experiments, Finn et al. [2] have confirmed that asphalt properties do influence pavement performance. However, the quantitative and consistent relationships between asphalt properties, asphalt-aggregate mixture properties, and pavement performance are too confounding to be established. Only qualitative relationships were established between asphalt properties and pavement performance. Monismith et al. [3] summarized these relationships as shown in Table 2-1.

Aging itself is a natural phenomenon rather than a failure. There could even be construction difficulties and tender mixes, partially due to not enough age hardening of binders. Binders with higher stiffness at high service temperature are generally used to improve rutting resistance. These experiences make age hardening of binders play a beneficial role in pavement performance. However, in a low service temperature environment, asphalt binders might become too hard and brittle due to excessive rate of age hardening and directly affect the thermal cracking of pavements. Although there is no strong direct evidence on how asphalt aging affects the fatigue cracking of and moisture damage to a pavement, the indirect influences can be recognized from the changes in stiffness and chemical composition during asphalt aging.

Table 2-1 Relationship between Asphalt Properties and Field Performance - 1950 to present

Distress Mode	Relative Asphalt Properties
Fatigue and Permanent Deformation	Related to stiffness of the asphalt -- information is inclusive because of strong interrelationships between these distress modes and pavement and environmental factors.
Thermal Cracking	More strongly related to asphalt properties than is fatigue or rutting; limiting viscosity and stiffness criteria have been proposed.
Aging	Chemical factors influence aging -- association more qualitative than quantitative.
Water Sensitivity	Chemical factors influence resistance to the action of water and water vapor.

Source: [3]

A decrease in penetration and an increase in viscosity are the direct signs of aging of an asphalt binder. For most of the cracked pavements, the recovered asphalts have a penetration value of less than 20 [4]. McLeod [5] and other researchers suggested that when the viscosity of asphalt exceeds 1×10^{10} poises at the lowest service temperature, the pavement will undergo thermal cracking. Asphalt cracking over a range of cooling rates has been related to stiffness and loading time. The stiffness limit temperature concept [6] has been proposed to control low temperature cracking in the field. Schmidt [7] suggested a limiting temperature as a criterion for cracking when the stiffness at 10,000 seconds reaches 1.4×10^{8} Pa (20,000 psi) at a cooling rate of 5 °C/hr. A stiffness limit of 300 MPa for a loading time of 2 hours has been used in the recent SHRP specifications [8]. All criteria are based on the principle that if an asphalt ages excessively it may become too hard to sustain the thermal strains induced by high temperature changes in the pavement material.

A laboratory procedure to accelerate the aging of asphalt is needed to screen out those asphalt binders that might have excessive aging in the expected service environment. The simulation of asphalt aging is also needed in order to investigate the other properties of the aged mixture, such as fatigue and rutting resistance.

2.2 The Mechanism of Asphalt Aging

Of the two main ingredients of asphalt concrete, aggregate is the more durable component. Though in some cases the aggregate might interact with the asphalt binder to affect the hardening of the binder, it is believed that the durability of asphalt concrete is controlled primary by the durability of the asphalt binder. Asphalt durability can be

defined as resistance to change in original properties with time. The term "asphalt aging" is commonly used in the literature to represent the change in asphalt properties caused by a number of factors such as oxidation, loss of volatile oils, and changes in molecular structure and chemical composition.

2.2.1 Asphalt Chemistry

Almost all paving asphalt cement used today is obtained from processing of crude oils. The composition of asphalt is complex and is different from source to source. Asphalts are recognized as complicated colloidal systems of hydrocarbon material that from a chemical point of view are largely unknown [9]. They have been arbitrarily divided into three fractions, namely asphaltenes, resins, and oils. These fractions can be separated by selective solvent and absorption techniques. It is generally considered that asphalt is a colloidal suspension of asphaltenes in an oily medium in which the resins act as peptizing agents to prevent congelation of the asphaltenes. Thus the continuous medium is oil, with the properties of an asphalt depending on the concentration of the dispersed phase and its degree of dispersion in the oily medium.

Although the composition tests based on fractional separation have not correlated consistently with field performance, some useful asphalt chemistry has been recognized as follows [10]:

(1) Asphalt has a significant heteroatom content. This includes nitrogen, oxygen, sulfur, vanadium, nickel, and iron.

(2) Heteroatoms play an important role in the physical properties of an asphalt. The polar heteroatom-containing compounds (functional groups) are

capable of intermolecular associations affecting such physical properties as boiling points, solubility, and viscosity. These polar compounds tend to be concentrated in the asphalt fraction of a crude oil.

(3) The molecular weight of asphalt compounds ranges from about 300 to 2,000. Yet, as a result of molecular associations, asphalt behaves as if it had a much higher molecular weight.

(4) Aging of an asphalt is associated with oxidation; an increase in the polar fractions on aging results, among other things, in increased asphalt viscosity.

(5) The composition, rheology, and durability of an asphalt are unique to the crude blend from which the asphalt is refined. Yet asphalts from many sources have performed well in roads.

The physical properties of an asphalt are determined by its chemical compositions. According to Corbett [11], the asphaltenes function as solution thickeners; fluidity is imparted by the saturate and naphthene aromatic fractions, which plasticize the solid polar aromatic and asphaltene fractions; the polar aromatic fraction imparts ductility to the asphalt; and the saturates and naphthene-aromatics in combination with asphaltenes produce complex flow properties in the asphalt.

2.2.2 Loss of Oily Components

In the colloidal system of asphalt cement, loss of the oily components (continuous phase) by volatility or absorption by porous aggregates results in hardening and embrittlement. Loss of oily components by volatilization is believed to occur in the

pugmill or drum mixer where the heated aggregate is mixed with the hot asphalt cement. During the short mixing time, the asphalt cement, which is in a very thin film, is exposed to air at a temperature that ranges from 135 to 160 °C (275 to 325 °F). The light ends of the asphalt components evaporate and are lost in the air. Current specifications limit the weight loss on TFOT or RTFOT to less than 1%. In an extensive investigation done by Welborn et al. [12], 19 out of 50 asphalts exhibit weight gain instead of weight loss after TFOT. The increase of weight is caused by the combination of molecules with atmospheric oxygen. In Welborn's study, the largest changes in weight are 0.12% and 0.87% on weight gain and weight loss, respectively. As recognized by refinery industries, a lower distillation temperature is used on the relatively heavy crudes (low API gravity) yielding a relatively higher percentage of asphalt and leaving more carry-over light ends in asphalt. Consequently, asphalts from heavy crudes exhibit weight loss, and those produced at high distillation temperature from light crude (high API gravity) exhibit weight gain after TFOT indicating less or no loss of oily components. Corbett and Merz [13] showed that the amount of the saturate fraction, which is the potentially volatile component remained virtually constant during 18 years of service in the well-known Michigan Road Test. As long as the amount of weight change is low, loss of oily components is probably not a significant contributor to asphalt hardening, particularly when the long-term aging is concerned.

2.2.3 Oxidation

The most important mechanism of age hardening is the change in the chemical composition of asphalt molecules from reaction with atmospheric oxygen. Petersen [14]

identified the chemical functionality in asphalt molecules normally present or formed on oxidative aging as shown in Figure 2-1 and found that ketones and sulfoxides are the major oxidation products formed during oxidative aging. Combined with atmospheric oxygen, the functional groups move from more nonpolar to more polar fractions. The reactivity of major components of asphalt were investigated. However, due to their operationally and procedurally defined nature, the results of composition tests in terms of the ratio of some components (such as the Rostler durability parameter) are not sufficiently precise to be used as an accurate predictor. Nevertheless, the formation of more polarities during oxidation and consequent molecular associations contribute to the age hardening of asphalt cement.

As in most chemical reactions the contact surface and temperature dominate the oxidation rate of an asphalt. Substantial oxidation takes place during mixing along with possible volatile loss. Oxidation continues, although at a much slower rate, while the asphalt concrete is processed through a surge or storage silo, transported to the paving site, laid, and compacted. After the asphalt pavement has cooled and been opened to traffic, the age hardening process continues at a significantly slower rate. The age hardening rate is dependent on the air void content and environment temperature. Although volatile loss and oxidation are two different mechanisms, they both result in the increase of asphalt viscosity. Consequently, viscosity is one of the major properties used to evaluate the age hardening of asphalt.

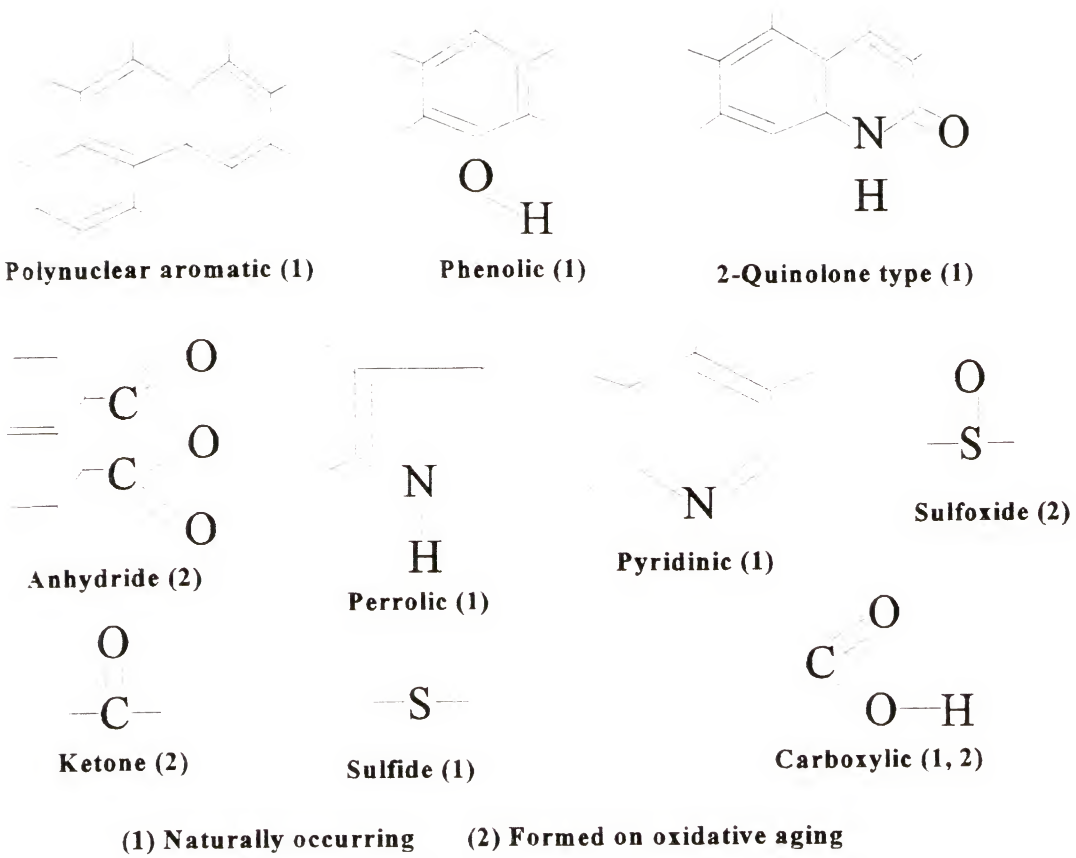


Figure 2-1 Chemical Functionality in Asphalt Molecules Normally Present or Formed on Oxidative Aging (Source: [14])

2.3 Evaluation of Asphalt Aging Characteristics

In order to evaluate the aging characteristics of asphalt, there are two major problems that need to be solved. First, there should be an appropriate laboratory aging procedure that can simulate the effect of aging under actual service conditions. Second, a property that can represent the durability of asphalt pavement should be determined as the evaluation parameter.

The aging of asphalts in the mixtures has been evaluated by such nondestructive tests as the dynamic modulus and such destructive tests as the indirect tensile test and the resulting tensile strength at break. The fabrication of specimens, the loading conditions, and the reproducibility make these mechanical tests too complicated for routine uses. Another approach is the measurement of viscosity on asphalt recovered from the mix. For this purpose, only a small amount of the asphalt is required, and both chemical and rheological properties can be investigated. However, complicated problems such as solvent hardening and partial recovery have been reported in the studies of recovering methods [15, 16].

2.3.1 Mechanical Tests on Asphalt Concrete

When other factors are the same, age hardening of asphalt cement results in an increase in stiffness of asphalt concrete. Evaluation of age hardening can be performed on asphalt concrete by measuring its mechanical properties before and after aging. The resilient modulus and indirect tensile strength are commonly used for this purpose.

Tensile strength of asphalt concrete is sensitive to the properties of asphalt in the mix and increases with the increase of asphalt viscosity due to aging. The indirect tensile

strength can be easily obtained by using the Marshall test equipment and a loading strip. The loading rate is 2 inches per minute, which is much higher than that of the thermal loadings. Previous studies at the University of Florida [17] found that the ultimate indirect tensile strength of Marshall specimens is around 400 psi at the loading rate of 2 inches per minute. A slower loading rate of 0.05 inch per minute has been used and a much lower strength reported in a recent AAMAS study [18]. As thermal cracking problems are concerned, the loading rate should be related to the cooling rate of the environment and therefore is a variable factor. Ruth et al. [19] suggested that as thermal cracking problems are concerned, fracture energy measured in the indirect tensile test is a good parameter. The horizontal strain has to be measured for the calculation of fracture energy. Tia et al. [20] showed that, as the asphalt ages, the fracture energy increases to a maximum and then decreases.

The values of resilient modulus can be used to evaluate the relative quality of materials as well as to generate input for pavement design or pavement evaluation and analysis. The modulus ratio has been selected by SHRP contractors [21] as the parameter for evaluation of aging of asphalt mixture. Although an indirect tensile mode of resilient modulus test has been adopted by ASTM (ASTM D4123), it is not intended for use in the specifications [22] possibly due to its complexity and poor reproducibility. Even though this information is very useful in the structural design of pavements, the appropriate method of preparation of specimens and the precision of tests are still in question. Thus, although the modulus ratio is a good evaluation parameter, Kim et al. [23] found in their study that the mixture properties were substantially different from those

measured from the field core samples, whereas the recovered asphalt properties were similar. A more recent SHRP report [24] showed that the effectiveness of the long-term mixture aging procedure by means of a forced-draft oven as proposed by the SHRP A-003A contractor could not be evaluated because the laboratory mixing and compaction methods used in this investigation did not represent field mixture and compaction. Low temperature properties in terms of creep stiffness of laboratory-produced mixtures were very different from those of field cores of the same mixture.

Properties of recovered binders from asphalt mixtures can be evaluated, and the relationship of binder properties and pavement performance can be established. It is believed that measurements from the recovered binders, as long as an adequate extraction/recovery procedure is used, are more reliable than those from mechanical tests on asphalt mixtures for the purpose of aging characterization.

2.3.2 Chemical Composition Tests on Asphalt Binders

The importance of asphalt chemical composition, although not well understood, cannot be disputed. The performance of asphalt as a binder in asphalt pavements is determined by its physical properties, which in turn are determined directly by chemical composition. As discussed in section 2.2.1, asphalt chemistry is complex; even with the analytical tools available, it would be almost impossible to identify and quantify all the components of even a single asphalt [10]. Asphalt has commonly been analyzed by separating it into fractions on the basis of solubility, absorption, or molecular size. Because these fractions are either operationally or procedurally obtained, the chemistry of the fractions has been only broadly defined. Solvent precipitation, as an example,

separates asphalt into different components by using different solvents. The asphaltenes of the same asphalt precipitated by Corbett method (ASTM D4124, n-Hentane) are very likely to be different from those precipitated by Rostler method (ASTM D2006, n-Pentane) not only in their polarity but also in their chemical reactivity. It will be much more complicated when these comparisons have to be applied to asphalts from different crude sources. As speculated by Goodrich et al. [10], the performance-related physical tests will continue to provide a reasonable way of describing asphalt quality without directly confronting the almost impossible task of describing a most complex chemical material.

As an identification tool of age hardening, size exclusion chromatography (SEC), such as gel permeation chromatographic (GPC) separation of asphalt constituents based on their associated sizes in dilute solutions, has been used as reported in the literature [10, 25]. Several researchers attempted to identify the degrees of asphalt aging by defining the GPC fractions as large, medium, or small molecular size (LMS, MMS, and SMS, respectively) based on calibration with polystyrene standards. Age hardening is indicated by an increase in the proportions of the large-size molecules. The inherent problems of SEC on asphalts make the interpretation of a chromatogram tricky and sometimes misleading. As described by Goodrich et al. [10], these problems include the effects of different solvents on molecular association, the selection of GPC columns, the use of different detectors, and the fact that the GPC measures the size of molecular association of asphalt components, rather than the true molecular size.

The infrared spectroscopic technique was used to measure changes in molecular structure of the binders due to aging, in terms of the changes in the amount of certain functional groups in them. The infrared absorption spectrum between 1600 cm^{-1} and 1900 cm^{-1} is of particular interest since it contains the absorption bands for the functional groups of carboxylic acids, ketones, and anhydrides [17, 20, 26]. However, Petersen [27] reported that the strongly associating polar functionalities present were never adequately identified or characterized because of several inherent problems such as overlapping, ill-defined absorption bands and the shifting of absorption bands from hydrogen bonding. In the previous research work done by Tia et al. [17, 20], it was concluded that the carbonyl ratio, which is a ratio of infrared absorbance at 1700 cm^{-1} and 1600 cm^{-1}, can be used to express the level of oxidation in an asphalt binder. A larger value of carbonyl ratio indicates a higher degree of age hardening. An increase of carbonyl ratio from about 0.3 of original asphalts to about 0.6 of aged sample was reported.

2.3.3 Physical Property Tests on Asphalt Binders

The penetration test and absolute viscosity test are traditionally used to compare the aging characteristics of different asphalts in terms of percent penetration retained and aging index, which are calculated by the following equations.

$$\text{Percent Penetration Retained (\%)} = 100 \times (pen_{residue} / pen_{original}) \quad (1)$$

$$\text{Aging Index} = AbsV_{residue} / AbsV_{original} \quad (2)$$

where

$pen_{residue}$: penetration of aged residue.

$pen_{original}$: penetration of original binder.

$AbsV_{residue}$: absolute viscosity at 60°C of aged residue.

$AbsV_{original}$: absolute viscosity at 60°C of original binder.

The current specifications for penetration graded asphalt [28] specify the penetration retained after TFOT to be larger than 55 % and 47% for 40-50 and 85-100 asphalt, respectively. The softer the asphalt, the lower the penetration retained allowed. For viscosity graded asphalt the aging index is limited to less than five [29].

The empirical nature and the insensitivity at high hardness levels are the drawbacks of the penetration test. The drawback of the absolute viscosity test is that it is usually limited to high temperatures of 60 °C or more. Due to the non-Newtonian nature of asphalt at service temperature, the rheological property of asphalt cannot be extrapolated by those obtained at higher temperatures. In previous studies at the University of Florida [17, 20], the Schweyer rheometer was used to measure the rheological properties of the aged asphalt at low temperatures. Constant power viscosity at 5 °C was measured and correlated to the direct observation of low temperature cracking to establish a viscosity limit.

At high temperatures (≥ 60 °C), most asphalt cements exhibit purely Newtonian viscous flow behavior in which rate of shear strain is proportional to stress. However, at low temperature most asphalts exhibit non-Newtonian flow behavior. In materials science, non-Newtonian materials are divided into several groups as shown in Figure 2-2 [30]. In a colloidal system such as asphalt, the oily component (continuous phase) acts as a lubricant. When an asphalt is subjected to a shear action, shear thinning behavior may be

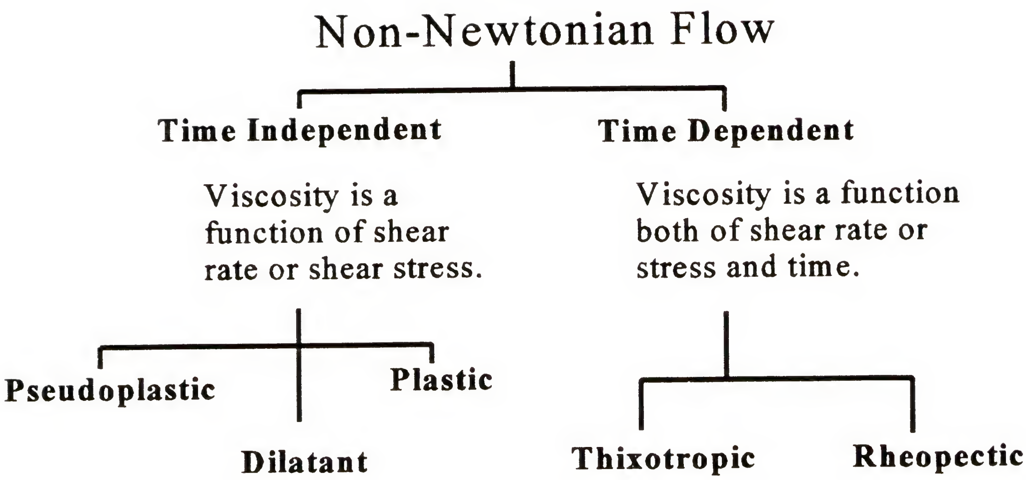


Figure 2-2 Classification of Non-Newtonian Flow (Source: [30])

exhibited. Thus, most asphalts exhibit pseudoplastic (shear thinning) at low temperatures. On the other hand, some clays exhibit dilatant flow behavior due to the formation of a connected structure among dispersed particles when subjected to shearing action [31].

Many equations have been proposed to describe the behavior of pseudoplastic and dilatant flow, but the most common one used is the empirical Power Law equation [30]:

$$\text{Shear stress} = K\ (\text{shear rate})^{C} \tag{3}$$

where

K = the consistency index

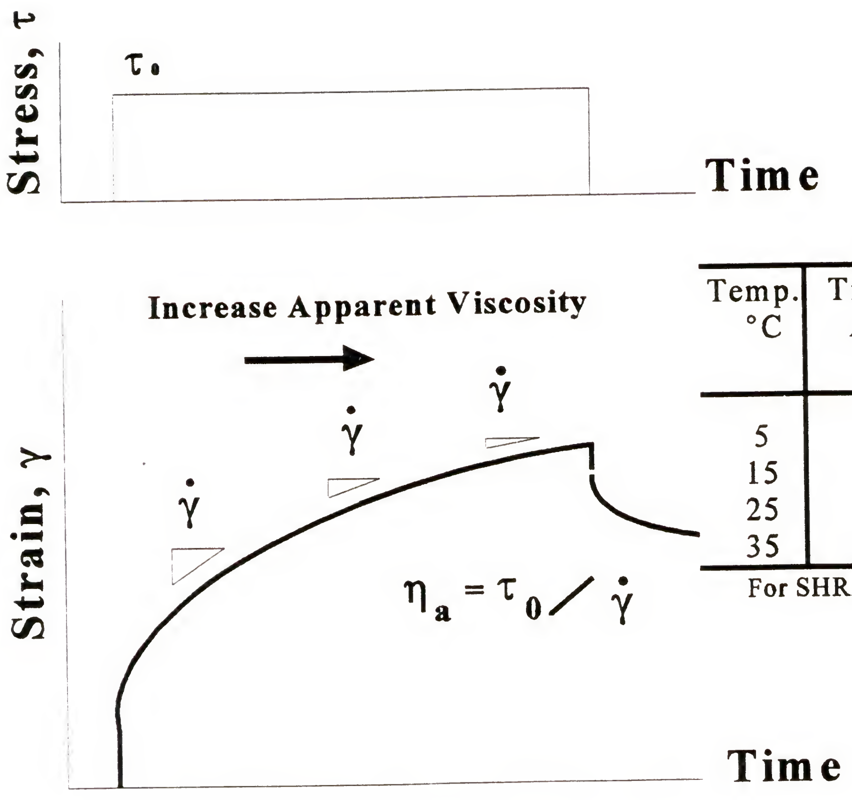
$$C = \frac{\log(\text{shear stress 1}) - \log(\text{shear stress 2})}{\log(\text{shear rate 1}) - \log(\text{shear rate 2})}$$

C = 1 for Newtonian

C < 1 for pseudoplastic

C > 1 for dilatant

In describing Schweyer's concepts, Tia and Ruth [32] defined shear susceptibility as the slope of the power law straight line when the log shear stresses are plotted against log shear rates and denoted it as "C," which is the same as C in Equation 3. The Schweyer rheometer test is a constant stress capillary flow test for asphalt cements performed at room temperature and below. To calculate viscosity from the test, it is necessary to get the stable strain rate at the specified stress level as shown in Figure 2-3. Recent SHRP researchers [8] showed that at loading times less than those given in the table of Figure 2-3, asphalt cement, even when loaded in the linear range, exhibits significant delayed elasticity such that shear rate is not constant. The experiences at the



Temp. °C	Time Required to Achieve Steady-State Flow
5	3 days
15	1 - 1/2 hours
25	5 mimutes
35	60 seconds

For SHRP Asphalt AAB-1

Figure 2-3 Change in Shear Rate and Calculation of Apparent Viscosity from Creep Data (Soucre: [8])

University of Florida seem to agree that shear susceptibility value is not very reproducible due to the relatively short loading time in the Schweyer rheometer tests. Therefore, although shear susceptibility is an important parameter to describe the rheological properties of asphalts, its relationship to pavement performance has not been established possibly because of the difficulties of rheological measurements at low temperature. Nevertheless, there is a general trend of reduction of shear susceptibility of asphalts on aging [17, 20].

Temperature susceptibility is the rate at which the consistency of an asphalt cement changes with a change in temperature and is a very important property of asphalt cement. For asphalts of the same grade, high temperature susceptibility is not desirable because it may mean an excessively high viscosity at low temperature and an excessively low viscosity at high temperature. Three different approaches for determining temperature susceptibility of asphalt cement have been used and are described as follow [33, 34]:

(1) Penetration index, *PI*

$$PI = \frac{20 - 500 \times A}{1 + 50 \times A} \tag{4}$$

Where

$$A = \frac{\log(PT_1) - \log(PT_2)}{T_1 - T_2}$$

PT_1, PT_2 = Penetration in 0.1 mm at T_1, T_2

T_1, T_2 = temperature in °C

(2) Viscosity-Temperature Susceptibility, $VTS\,(T_1 - T_2)$:

$$VTS\,(T_1 - T_2) = \frac{\log(\log(V_2)) - \log(\log(V_1))}{\log(T_1) - \log(T_2)} \qquad (5)$$

Where

T_1, T_2 = temperature in degrees Kelvin

V_1, V_2 = viscosity in centipoise at T_1 and T_2

(3) Penetration-Viscosity Number, $PVN_{(25\text{-}135)}$:

$$PVN_{(25\text{-}135)} = \frac{1.5 \times (A - \log(V_{135})}{A - B} \qquad (6)$$

Where

$A = 4.25800 - 0.79674 \log(P_{25})$

$B = 3.46289 - 0.61094 \log(P_{25})$

V_{135} = viscosity in centistoke at 135 °C

P_{25} = penetration in 0.1 mm at 25 °C

Or, Penetration-Viscosity number, $PVN'_{(25\text{-}60)}$:

$$PVN'_{(25\text{-}60)} = \frac{-1.5(6.4890 - 1.59\log(P_{25}) - \log(V_{60}))}{1.05 - 0.2234\log(P_{25})} \qquad (7)$$

where

V_{60} = viscosity in poises at 60 °C

P_{25} = penetration in 0.1 mm at 25 °C

All these temperature susceptibility parameters are obtained from consistency measurements not only at different temperatures but also at different stress levels. These parameters are confounding with the change of shear susceptibility on age hardening especially when a lower temperature range is used. Roberts et al. [33] noted that the *PI* changes on aging, whereas the $PVN_{(25\text{-}135)}$ remains substantially the same. McLeod [5] also claims that *PVN* remains the same after aging and is the best parameter for temperature susceptibility. Recent studies at the University of Florida [17] used the constant power viscosity-absolute temperature (°K) relationship in the log-log plot to define the temperature susceptibility according to the following equation:

$$log(\eta_{100}) = \beta_0 - \beta_1 \, log(T) \tag{8}$$

where

η_{100} = constant power viscosity at T.

T = absolute temperature in °K.

β_0 = the intercept of regression line.

β_1 = the slope of regression line.

Absolute viscosity is considered to be a constant power viscosity η_{100} at 60 °C, according to the assumption that asphalt is a Newtonian flow at that temperature. β_1 is a parameter corresponding to temperature susceptibility. A higher β_1 value means more temperature susceptible. Florida's experiences [35] showed that β_0 equals 172 and β_1 equals 67.1, for a typical AC-30. As asphalts age, the log viscosity versus log temperature line is shifted parallel. The line shifts farther when the asphalt ages further.

Page et al. [36] reported that there was a fairly linear relationship between the logarithm of the test parameter and the logarithm of pavement age (in days). When constant power viscosity was used as the test parameter, the logarithm of pavement age (in days) is related to the amount of shifting in the log-log plot of constant power viscosity versus absolute temperature. The relationship can be expressed as follows:

$$log(\eta_{100}) \;=\; \Delta\beta + \beta_0 - \beta_1 log(T) \tag{9}$$

in which

$$\Delta\beta \;=\; A + B \times log(\,days) \tag{10}$$

Equations 9 and 10 have been used in the computer program REhabilitation Design of Asphalt Pavement Systems (REDAPS Version 2), developed by Ruth et al. [37] for the Florida Department of Transportation.

2.4 Recovery of Asphalt Binders from Aged Mixtures

To study the changes occurring in asphalt as it hardens in the hot-mix plant or roadway and to determine the asphalt content of cores and mixes, it is necessary to extract the asphalt from the aggregate and to recover the asphalt from the extracted solution. This can be done by the standard test methods as specified in ASTM D2172 [38] and ASTM D1856 [39]. A round-robin test conducted by AASHTO in 1989 shows that the coefficient of variance of the viscosity of recovered binders was about 25%. In earlier years it has been as high as 42% [40]. There seem to be three main areas from where errors are likely to stem:

(1) The solvent has some hardening effect on the asphalt that increases with temperature and time of exposure.

(2) Asphalt is not completely removed from the aggregate.

(3) The solvent is not completely removed from asphalt during recovery. This results in viscosities that are lower than the true value.

In ASTM D2172 [38], the paving mixture is extracted with specified solvents using the extraction equipment applicable to the particular method. The allowable solvents and extraction methods are shown in Table 2-2 and Table 2-3. Stroup-Gardiner et al.[41] compared the asphalt contents and showed no statistical difference among the centrifuge, reflux, and vacuum extraction methods, regardless of the type of solvent used for the test. However, when the properties of extracted asphalt cement are required, only the solutions obtained by the ASTM D2172 Method A (centrifuge method) is allowed in ASTM D1856 (Abson Method). This is because "there is some experimental evidence that the recovered asphalt may have slightly lower penetration values when recovered from solutions obtained from hot extraction methods" [39]. Centrifuge extraction produces a large amount of solvent, which extends the process time for primary distillation by the subsequent Abson recovery method. Therefore, a lot of agencies, including FDOT, use reflux extraction, which is not allowed in the ASTM procedure, in the routine extraction/recovery procedure.

To investigate solvent aging, Burr et al. [15] ran extensive experiments on differing concentrations of dissolved asphalt using a number of solvents and various levels of light and oxygen exposure. The mechanism of solvent aging is still unclear, although it

Table 2-2 Solvents Used in ASTM D2172

Solvent	Formula	Density	B. P.[1] °C	TLV[2], ppm
Benzene	C_6H_6	0.8756	80.1	1
Methylene chloride	CH_2Cl_2	1.3266	40.0	200
Trichloroethylene	C_2HCl_3	1.4642	87.0	100
1,1,1-Trichloroethane	$C_2H_3Cl_3$	1.3390	74.1	350
Toluene[3]	$C_6H_5CH_3$	0.8669	110.6	100

Note 1. Boiling Point.

2. Threshold Limit Value as established by the American Conference of Governmental Industrial Hygienists. The TLV is a time weighted average for an exposure period of 8 hours per day, 5 days per week.

3. Toluene (Methylbenzene) is not listed in ASTM D2172 but generally used.

Source: [38]

Table 2-3 Extraction Methods Used in ASTM D2172

Method	Extraction Type	Hot or Cold Extraction
A	Centrifuge	Cold
B	Reflux	Hot
C	Reflux	Hot
D	Reflux	Hot
E	Vacuum	Cold

Source: [38]

seems to occur in all solvents and to varying degree in all asphalts. The choice of extraction solvent is important in determining how much of the asphalt is extracted by a given methods. Burr et al. [42] reported that Method A typically leaves 2 to 4 percent of the asphalt on the aggregate when trichloroethylene (TCE) is the extraction solvent and Method B leaves much more asphalt unextracted because of the poor solvent contact.

Cipione et al. [16] studied the incomplete extraction of asphalt from aggregate by using lots of different solvents and found that no method could remove all the asphalt. It was also noticed that asphalt components that are difficult to remove probably affect adhesion but not bulk properties. If only the bulk properties of binders are required, many solvents and methods would be adequate.

The recovery of asphalt from extracted solution is done commonly by means of the Abson method (ASTM 1856). Due to the inadequate temperature control of the equipment and its sensitivity to temperature variation, the variance of viscosities of the recovered asphalts might be occasionally high. Recently the rotary vacuum evaporator (Rotavapor) was used in place of the conventional Abson method because (1) the vacuum in the evaporator enables a more complete separation of the solvent and minimizes the effects of oxidation of the asphalt and (2) the rotation of the evaporating flask enables a more even heating of the solution and better control of its temperature. Although this method of asphalt recovery has not yet been standardized, the ASTM D4887-89 standard (for Preparation of Viscosity Blends for Hot Recycled Bituminous Materials) stated that the Abson method might be modified by using a rotary evaporator. Some agencies such as Georgia Department of Transportation and Florida Department of Transportation have

developed the recovery method using the Rotavapor machine [43, 44]. A further validation process was performed in this study to compare the differences between different combination of extraction/recovery procedures.

2.5 Laboratory Simulation of Asphalt Aging

Asphalts undergo two substantially different aging processes in its service life. It is subjected to high temperature and high degree of air exposure during its relatively short production time (short term aging), and then to the environment at a relatively lower temperature and air void content for a long time duration (long term aging). A variety of methods have been proposed and investigated to simulate the aging characteristics of asphalt during mixing as well as field service. A tabulated review has been made by Welborn [45] as shown in Table 2-4. Ideally, asphalts hardened by a laboratory aging method should be similar to those aged in actual service environments. Furthermore, the method should be reasonably simple in order to be used as a routine control test. The sample size of aged residue should be reasonable to allow for necessary tests.

The average thickness of asphalt film of a dense grade asphalt mixture is around 10 to 20 micron depending on the asphalt content and gradation of aggregate. Although it is closer to the real situation, microfilm aging as listed in Table 2-4 produce aged residue only big enough for chemical composition test or microviscometer test, and thus are not considered to be adequate.

The major characteristics of short term aging are the high temperature and large reaction surface which result in a high oxidation rate and possible evaporation of oily components. The most successful simulation methods are the thin film oven test (TFOT) [

Table 2-4 Laboratory Accelerated Tests and Evaluation Methods to Determine Asphalt Durability

Date	Investigator	Test Method	Evaluation Method
1903	Dow	30 hr, 400 °F	Change in weight, penetration of residues
1903	Dow	Mixture aged for 30 min., 300 °F	Recovered asphalt, change in penetration
1937	Nicholson	Air blowing, 15 min., 425 °F	Penetration, ductility
1937	Rashig and Doyle	Air blowing, 15 min., 400 °F	Change in penetration
1937	Hubbard and Gollumb	Mixture, time and temperature varied	Recovered asphalt, change in penetration
1939	Lang and Thomas	Mixture, oven and outdoor aging	Change in mix properties, abrasion, strength, etc.
1940	Shattuck	Mixture, oven aging 30 min., 325 °F	Recovered asphalt, penetration, ductility, soft point
1940	Lewis and Welborn	1/8" film oven test, 5 hr., 325 °F (TFOT)	Change in weight, penetration, ductility
1946	Lewis and Halstead	1/8" film oven test, 5 hr., 325 °F (TFOT)	Change in weight, penetration, ductility
1952	Pauls and Welborn	Mixture, oven aging, TFOT	Compressive strength, residues
1955	Griffin et al.	Shell microfilm test, 5 μm, 2 hr., 225°F	Viscosity before and after aging, aging index
1955	Heithaus and Johnson	Road tests, lab aging, microfilm	Recovered asphalts, microfilm aging index
1961	Traxler	TFOT and microfilm, 15 μm, 2 hr., 225 °F	Microviscosity at 77 °F compared
1961	Halstead and Zenewitz	TFOT and 15 μm film, 2 hr., 225 °F	Microviscosity at 77 °F compared
1963	Hveem et al.	Shell microfilm test, modified 20 μm, 24 hr., at 210 °F	Microviscosity at 77 °F before and after aging
1969	Hveem et al.	RTFOT and TFOT	Viscosity of RTFOT, TFOT, and recovered asphalts compared
1981	Schmidt and Santucci	RTFOT, 20 μm film, 210 °F	Microviscosity of residue
1981	Kemp and Predoehl	Tilt Oven durability test, 168 hr., 235 °F (California Tilt Oven)	Penetration, 77 °F ductility

Source: [45]

46] and rolling thin film oven test (RTFOT) [47]. These two methods are recognized to give the same aging effect and can be used to predict the degree of age hardening of an asphalt cement during conventional hot-mixing at 150 °C (300 °F) as indicated by penetration or viscosity measurements. Page et al. [36] found that the effect of plant mix temperature on hardening were proportional to different TFOT temperatures up to 185 °C (365 °F).

The aged-residue viscosity-graded specification (AR grade) has been used by the Pacific Coast states [48] to avoid using of nondurable asphalts. However, it is believed that some asphalts especially those refined from heavy crudes were affected more by mixing than in situ aging and vice versa. Therefore Santucci and Schmidt [49] suggested that it might be dangerous to predict long term durability from short term hardening characteristics. In a study by Kemp and Predoehl [50], the RTFOT test was modified to heat the RTFOT samples at lower temperature with the oven slightly tilted to prevent asphalt build-up. Penetration at 25 °C (77 °F), absolute viscosity at 60 °C (140 °F) and ductility at 25 °C (77 °F) were measured on the residues as the predicted durability characteristics of the asphalts after two years of hot desert environment. Higher viscosity asphalts tend to have less movement during the rolling process and to have a reduced oxidation rate. This is one of the possible drawbacks of the California Tilt Oven.

Durability studies at the University of Florida found that it is possible to simulate the effects of aging during service as well as that of hot mixing process by using the TFOT or RTFOT at a higher temperature [17, 20]. A criticism for this method is its higher

process temperature which may unrealistically produce a large volatile loss to obtain sufficient hardening.

Recent SHRP related study [3] listed the promising methods as shown in Table 2-5. For the simulation of long term aging, Petersen [51] reported some evidence to suggest that the mechanism of oxidation at high temperatures is different to that at low temperatures. Button et al. [52] described two major mechanisms of aging at high temperatures as follows:

(1) Volatilization: At higher temperatures, light constituents of asphalt evaporate, producing unrealistic changes in the chemistry of the oxidation reactions when compared with field-aged asphalts.

(2) Dehydrogenation: The high molecular constituents are believed to dehydrogenate at high temperature and a large percentage of oxygen consumed is discharged in the form of water vapor and other gases, which does not occur at normal service temperatures.

The pressure oxygen treatment procedure in Table 2-5 was originally developed by D. Y. Lee [53] with the name of Pressure Oxygen Bomb (POB). Pure oxygen was pressurized under different levels to accelerate oxidative aging of asphalt binder at 60 °C. Temperature was maintained by a water bath surrounding the pressurized vessel bath for a duration up to a week. WRI evaluated the POB and modified it for SHRP [52]. The major change of WRI modified model is that the pure oxygen was replaced by air for safety reason and the pressure of the reaction vessel was specified to be 2.07×10^{6} pascals (300 psi). SHRP researchers [54] decided to raise the test temperature and use the name

Table 2-5 Age Conditioning Procedures Evaluated in SHRP Related Studies

Type	Method	Simulation field condition	Application of method	Existing experience
Short Term	Extended heating	Good data from AAMAS	Similar to TFOT	Little on mixes
	Extended mixing	Simulates plant mixing	Similar to RTFOT	Little on mixes
	Microwave heating	Not the same	May promote structuring	Very little
Long Term (1- 10 years)	Extended heating	Significant aging but at high temperatures	Similar to extended TFOT or RTFOT	Little on mixes
	Pressure oxygen treatment	Significant aging at low temperatures	Simulates aging due to oxidation	Little on mixes
	Modified triaxial cell	Difficult to assess	Potential to condition with several "fluids"	None on mixes

Source: [3]

of Pressure Aging Vessel (PAV). The aging period is shortened to 20 hours but the conditioning temperature was raised to about 100 °C. A precision oven is used to maintain the test temperature.

The PAV process is proposed to simulate long term aging at service temperature. By applying a higher oxygen content through increasing air pressure at elevated temperature, oxidation of asphalt can be accelerated within a short time. Using PAV on compacted mixtures, Bell et al. [21] encountered the problem of sample disruption when pressure was released at the end of PAV process and lower resilient modulus was obtained in their study. SHRP has proposed a procedure, in which standard RTFOT residues are transferred into TFOT pans and put into the vessel under 300 psi for 20 hours at 90, 100, or 110 °C depending on the service environment [54].

An appropriate aging process must be able to harden a wide variety of asphalts in the same orders as do field exposures. Beaton and Sherman [55] reported that the asphalts in asphalt concrete exposed at 60 °C (140 °F) in the laboratory hardened in the same order as they did in the experimental pavements. Recent studies at the University of Florida [17] also found that Marshall specimens exposed to a 60 °C forced-draft oven for 90 days can simulate six to nine years aging on the roads in Florida environment.

In its nature of reaction with atmospheric oxygen, the hardening rate of asphalt pavement is largely dominated by the air void content of the pavement. When considering air void content at some selected age, Page et al. [36] concluded that the recovered asphalt viscosity or penetration usually indicated harder asphalts for samples with higher air voids content. Due to the significant effect of air void content of the specimens, it is

believed that accelerated aging in the laboratory could be obtained if loose mixtures are used either in the UV chamber or forced-draft oven.

A forced draft oven is selected by SHRP researchers [58] to extend heating the laboratory-produced asphalt mixtures. The fresh mixed samples are subjected, in their loose states, to short term oven aging (STOA) at 135 °C for four hours with mixing at each hour interval. For the long term oven aging (LTOA), the STOA aged mixtures are compacted and then subjected to an 85 °C forced draft oven for five days.

CHAPTER 3
RESEARCH PROGRAM AND INSTRUMENTATION

3.1 Introduction

The major objective of this study is to find a rational method to predict asphalt durability during service in Florida's pavements. Asphalt cements (conventional and modified), that are commonly used in Florida were subjected to the proposed accelerated aging processes and their aged residues were tested for comparison of aging severity. The effects of different processes were obtained and their relationships were established. Loose mixtures made of the same binders were aged in the UV chamber and forced-draft oven for different durations, and the binders of the aged mixtures were recovered and tested. Marshall specimens aged under natural sunlight up to four years were evaluated and test data of some paving projects were analyzed to correlate the effects of laboratory aging to those of field aging under Florida's condition. This chapter describes the detailed research program and instrumentation.

3.2 Asphalt Extraction and Recovery Methods

To evaluate the new rotavapor procedure, a testing program for comparing different combination of extraction/recovery procedures was conducted. Asphalts were extracted from the same mixtures using three different extraction and three recovery methods as listed in Figure 3-1. The three different extraction methods used are:

(1) the centrifuge method, ASTM D2172 Method A.

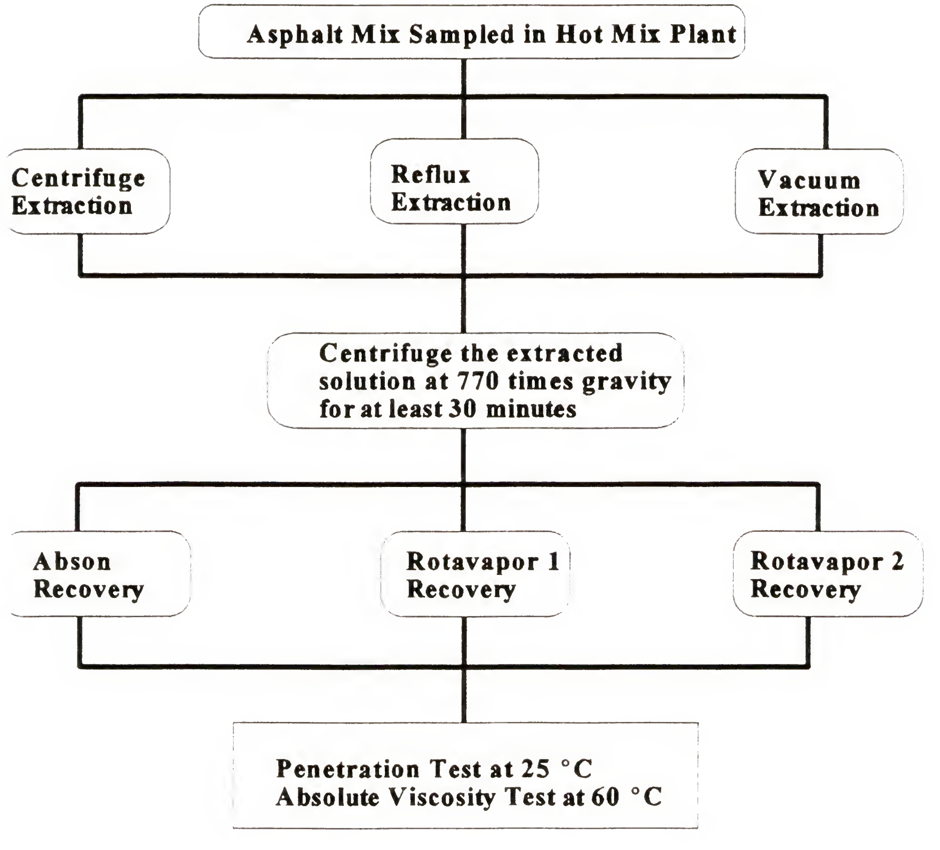


Figure 3-1 Testing Program for Asphalt Extraction and Recovery Methods

(2) the reflux method, ASTM D2172 Method B.

(3) the vacuum extractor, ASTM D2172 Method E-II.

The extracted solutions were centrifuged at a force of higher than 770 times gravity for at least 30 minutes according to ASTM D1856 to eliminate mineral matter. A large-capacity floor-model centrifuge as shown in Figure 3-2 was used for this purpose. Four 250 ml centrifuge bottles were loaded in a swinging bucket rotor which was installed in the centrifuge machine. With a rotating radius of 19.7 cm, a relative centrifuge force (*RCF*) of 770 gravity was produced by a rotating speed of 1,876 RPM as calculated in the following equation [59].

$$RCF \;=\; 0.00001118 \times 19.7 \times 1876^2 \;=\; 770g$$

The three different recovery methods used are:

(1) the Abson method, ASTM D1856.

(2) the Rotavapor 1.

(3) the Rotavapor 2.

The schematic representation of Rotavapor 2 as shown in Figure 3-3 is the recovery method according to the "Standard Test Method for Recovery of Asphalt from Solution Using the Rotavapor Apparatus, Draft 7" [43]. The Rotavapor 1 is the modified method, which does not use the nitrogen purge but increases the rotation speed, as suggested by the investigators for its simplicity. The solvent used in this study is trichloroethylene which is used in the routine reflux/Abson procedure of FDOT. Penetration test at 25 °C and absolute viscosity tests at 60°C were used as the evaluation

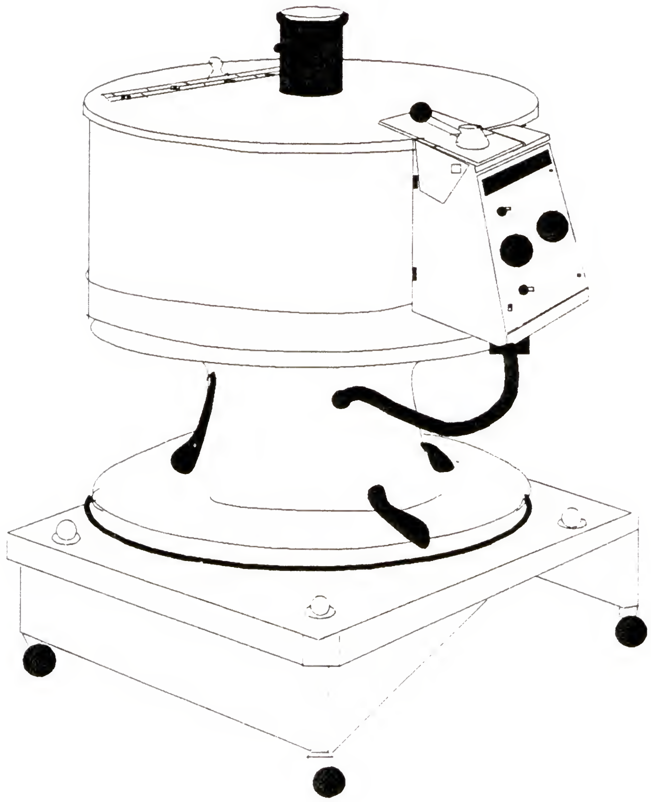


Figure 3-2 The Model K Centrifuge Manufactured by International Equipment Company

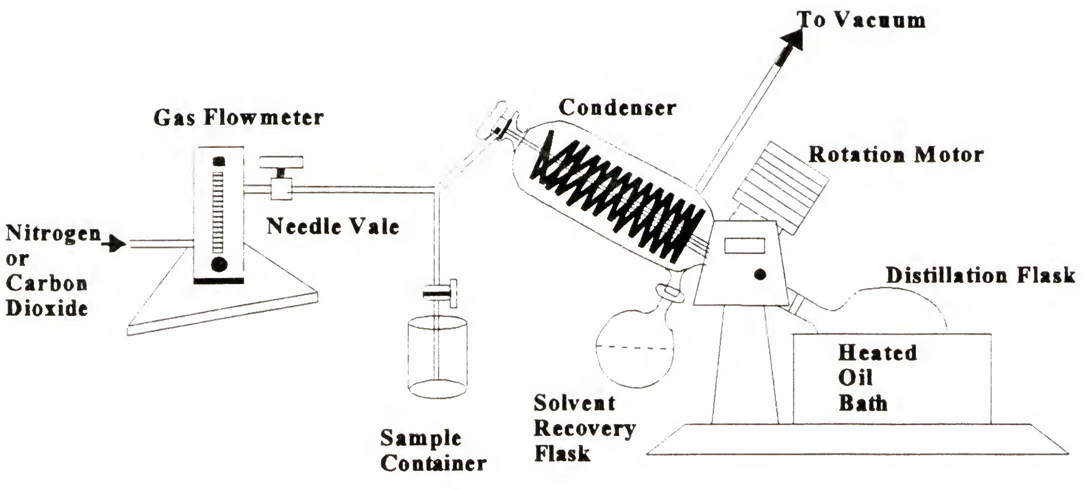


Figure 3-3 Schematic Representation of Rotavapor Apparatus and Recovery System

parameters to compare the differences among different extraction/recovery methods. A complete factorial experiment was conducted using four replicate samples per extraction/recovery combination. This amounts to a total of ($3 \times 3 \times 4 =$) 36 samples to be prepared and tested.

3.3 Investigation of Different Aging Methods on Asphalt Cements

Figure 3-4 shows the testing program of subjecting asphalt cements to different accelerated laboratory aging procedures. Five different asphalts acquired from three refinery sources as listed in Table 3-1 were used for evaluation of the differences between the various aging methods and their relationships with one another. For each selected binder, the following aging processes were used:

(1) Conventional TFOT at 140, 163 and 185 °C.

(2) Modified TFOT using 25g samples at 140, 163, and 185 °C.

(3) Conventional TFOT at 163 °C for 10 and 15 hours.

(4) UV chamber at 60 °C for 7, 14 and 28 days (on TFOT-aged residues).

(5) California Tilt Oven for 24, 72 and 168 hours.

(6) Pressure Aging Vessel using 300 psi for 20 hours at 90, 100, and 110 °C (on TFOT-aged residues).

These methods sum up to a total of 17 levels of age hardening as listed in Table 3-2. Two replicate tests were performed for each condition. This amounts to a total of ($5 \times 17 \times 2 =$) 170 samples to be tested.

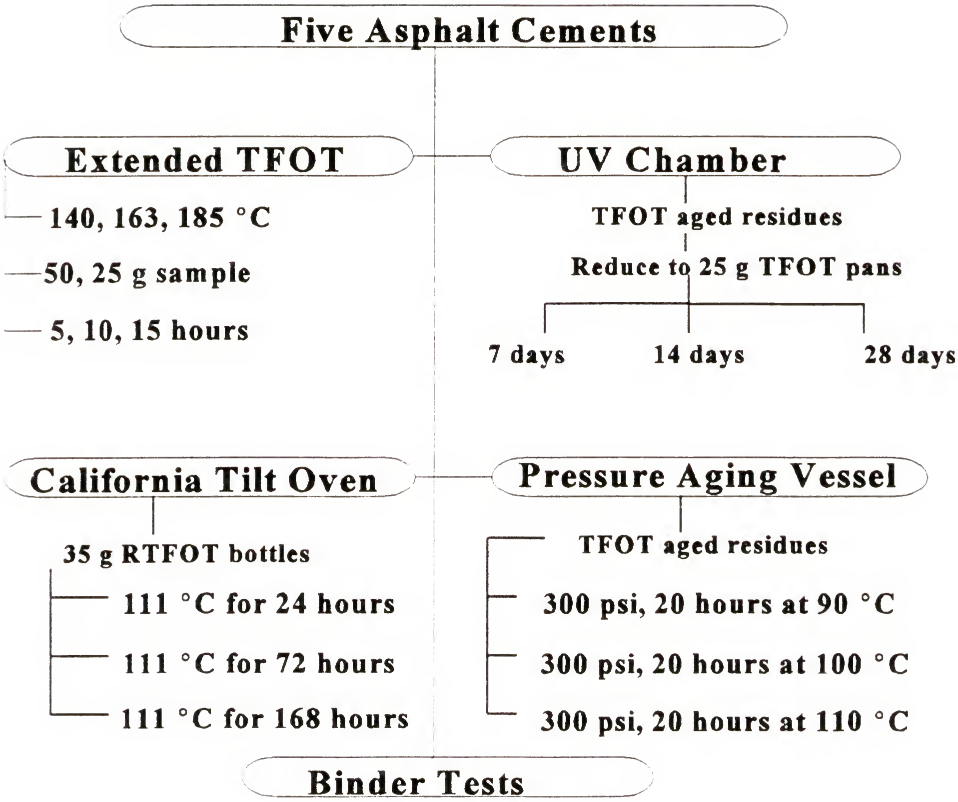


Figure 3-4 Testing Program for Investigation of Different Aging Methods on Asphalt Cements

Table 3-1 Asphalt Binders Used in This Study

Unmodified Binders		
Refinery Source	Grade	Abbreviation
Coastal	AC-30	CT30
Amoco	AC-30	AM30
Amoco	AC-20	AM20
Mariani	AC-30	MA30
Mariani	AC-20	MA20
Modified Binders (use Coastal AC-30 as base asphalt)		
Modifier	Dosage (%)	Abbreviation
#80 fine ground tire rubber	5	GTR
carbon black	10	CB
styrene ethylene butylene styrene	5	SEBS
ethylene vinyl acetate	5	EVA
styrene butadiene rubber	3.5	SBR

Table 3-2 Laboratory Asphalt Aging Processes Investigated in This Study

Extended TFOT	Abbreviation
TFOT, 50 g, 140 °C, 5 hours	TL
TFOT, 50 g, 163 °C, 5 hours	TS
TFOT, 50 g, 185 °C, 5 hours	TH
TFOT, 50 g, 163 °C, 10 hours	TF10
TFOT, 50 g, 163 °C, 15 hours	TF15
TFOT, 25 g, 140 °C, 5 hours	TLM
TFOT, 25 g, 163 °C, 5 hours	TSM
TFOT, 25 g, 185 °C, 5 hours	THM
UV Chamber	**Abbreviation**
TS+UV, 60 °C, 7 days	UV7
TS+UV, 60 °C, 14 days	UV14
TS+UV, 60 °C, 28 days	UV28
California Tilt Oven	**Abbreviation**
111°C, 24 hours	C24
111 °C, 72 hours	C72
111 °C, 168 hours	C168
Pressure Aging Vessel	**Abbreviation**
TS+PAV, 300 psi, 90 °C, 20 hours	P90
TS+PAV, 300 psi, 100 °C, 20 hours	P100
TS+PAV, 300 psi, 110 °C, 20 hours	P110

3.3.1 Extended TFOT

A thin film oven is shown in Figure 3-5. The conventional test method as described in ASTM D1754 is performed at 163 °C for 5 hours using 50-g asphalt samples in the standard TFOT pan. The process is extended in this study by using a higher temperature, a thinner film and for longer times. A lower temperature of 140 °C was selected due to the possible reduction of mixing temperature in a drum mix plant. The 185 °C exposure was used to enlarge the differences between different asphalt binders through a more severe condition of aging. These three equally separated temperatures also cover the possible temperature range used in the mixing of asphalt concrete in a hot mix plant. A thinner film of 1.6 mm was fulfilled by using 25-g asphalt sample in the TFOT pans.

3.3.2 Ultraviolet Chamber

An ultraviolet chamber shown in Figure 3-6 which was developed at the University of Florida [20] was used in this study. The chamber was made from 3/8 inch plywood in the shape of a trapezoidal box with a 4'2" × 3'9 1/2" rectangular base and a height of 1'10". The two sides of the chamber were hinged to permit access into the chamber and the interiors of these two hinged sides were used to mount four lamp assemblies, each assembly carrying two lamps. The roof of the chamber was used to mount one more lamp assembly carrying two lamps. Totally, ten 40-watt fluorescent UV-B lamps (URB-313) were used in the chamber. Two lamps was replaced and the other eight lamps were rotated at intervals of 360 hours as shown in Figure 3-6 in order to avoid the reduction of UV strength with time. Temperature in the chamber was maintained at 60 °C through the

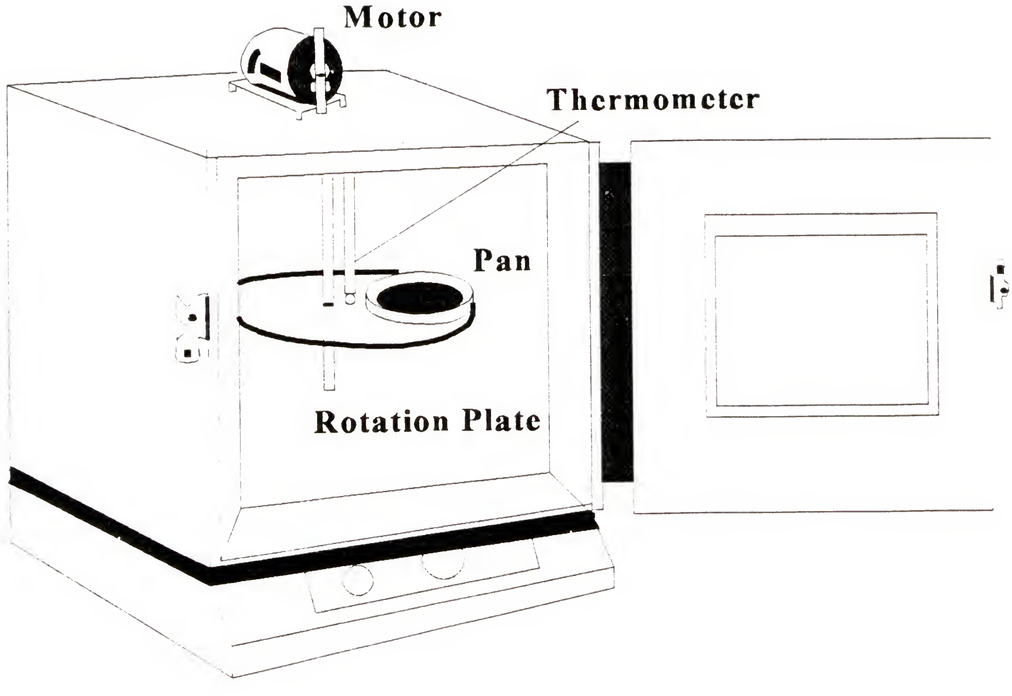


Figure 3-5 Thin Film Oven

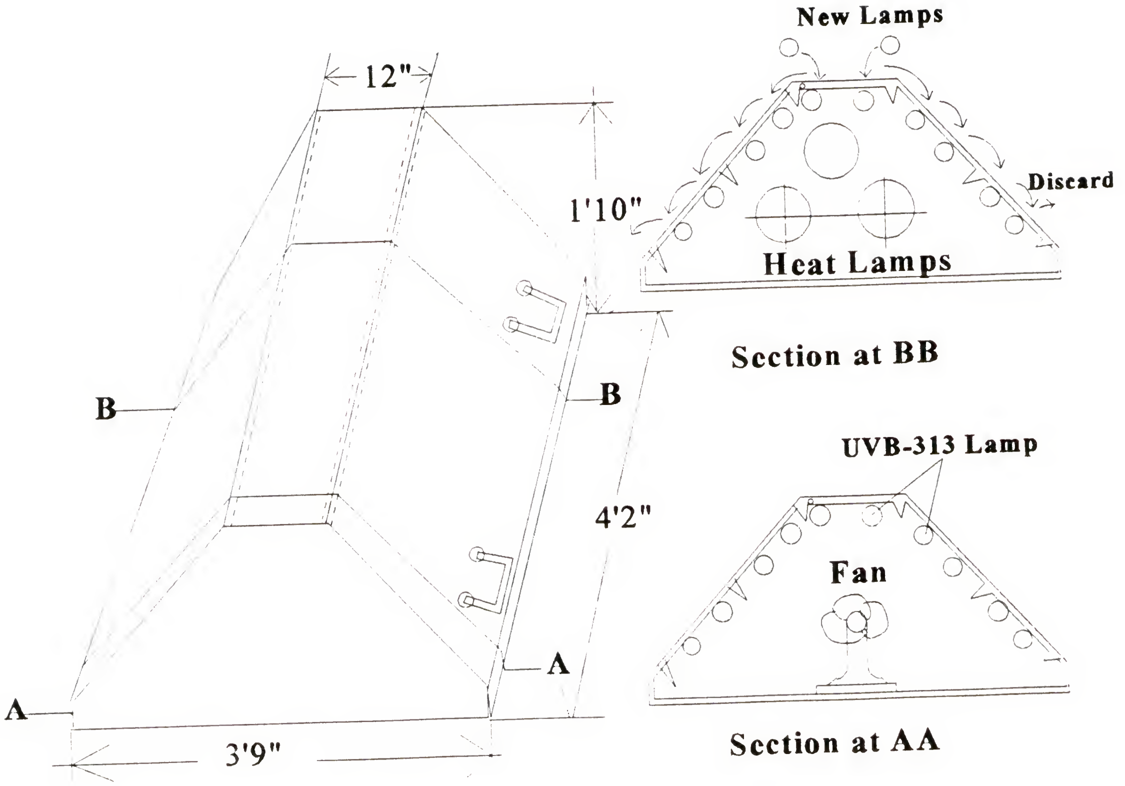


Figure 3-6 Ultraviolet Chamber

use of a thermostat, infrared heatlamps and a circulation fan on the vertical endsides of the chamber.

The residues from the conventional TFOT process were reduced to 25 g samples and placed in TFOT pans. The TFOT pates containing 25 g residues were then placed in the 60 °C UV Chamber for durations of 7, 14, and 28 days.

3.3.3 California Tilt Oven

A Rolling Thin Film Oven (RTFOT, ASTM D2872) as shown in Figure 3-7 was used in this study. The bottle carriage assembly rotates at a rate of 15 ± 0.2 RPM. The air flow was set at a rate of 4000 ± 200 ml/min. In the process of California Tilt Oven [56], the oven was positioned so that the horizontal axes of the glass containers is tilted by 1° higher in the front of the oven as shown in Figure 3-7. The RTFOT bottles with 35 g samples were heated at the temperature of 111 °C for 24, 72, and 168 hours. After the process, the RTFOT bottles were put into a 160 °C oven for 20 minutes in order to obtain sufficient fluidity to pour the aged residues out of the bottles.

3.3.4 Pressure Aging Vessel

The SHRP proposed Pressure Aging Vessel which is the SHRP Product 1003[54] was investigated in this study. Figure 3-8 shows the schematics of the PAV test system consisting of a pressure vessel, pressure controlling devices, temperature controlling devices, pressure and temperature measuring devices, and a temperature readout device. Two systems which are different in the capping design of the vessel and the heating oven were used in this study. The old system uses an eight-bolt capped vessel and a conventional oven. A longer preheating time of about four hours was used in this system.

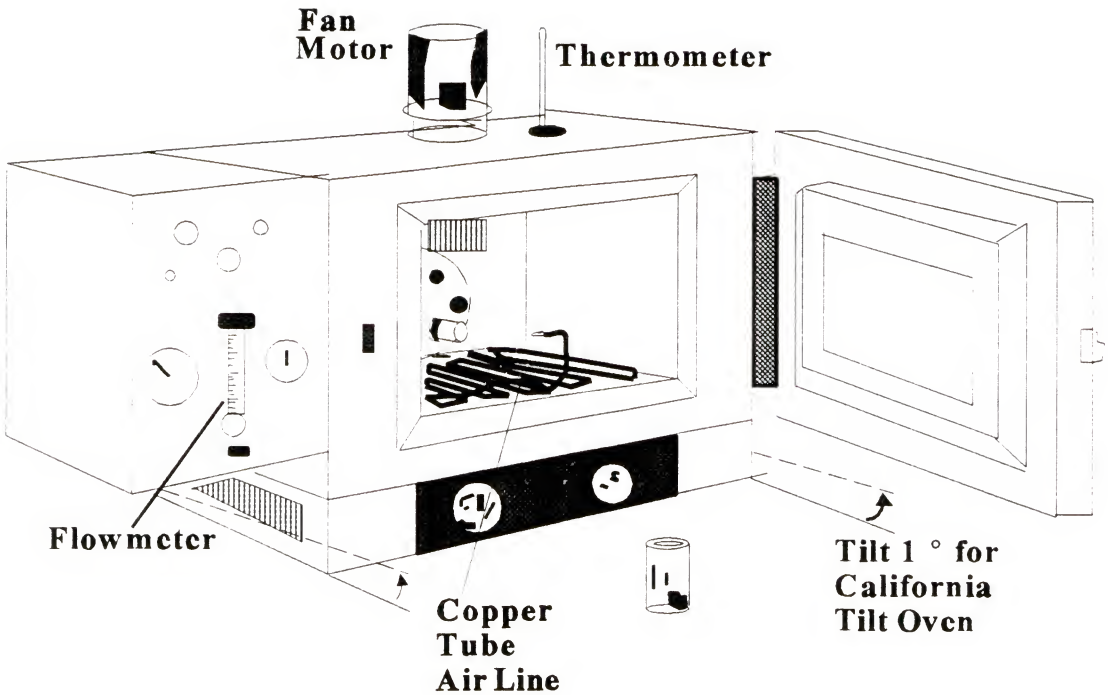


Figure 3-7 Rolling Thin Film Oven

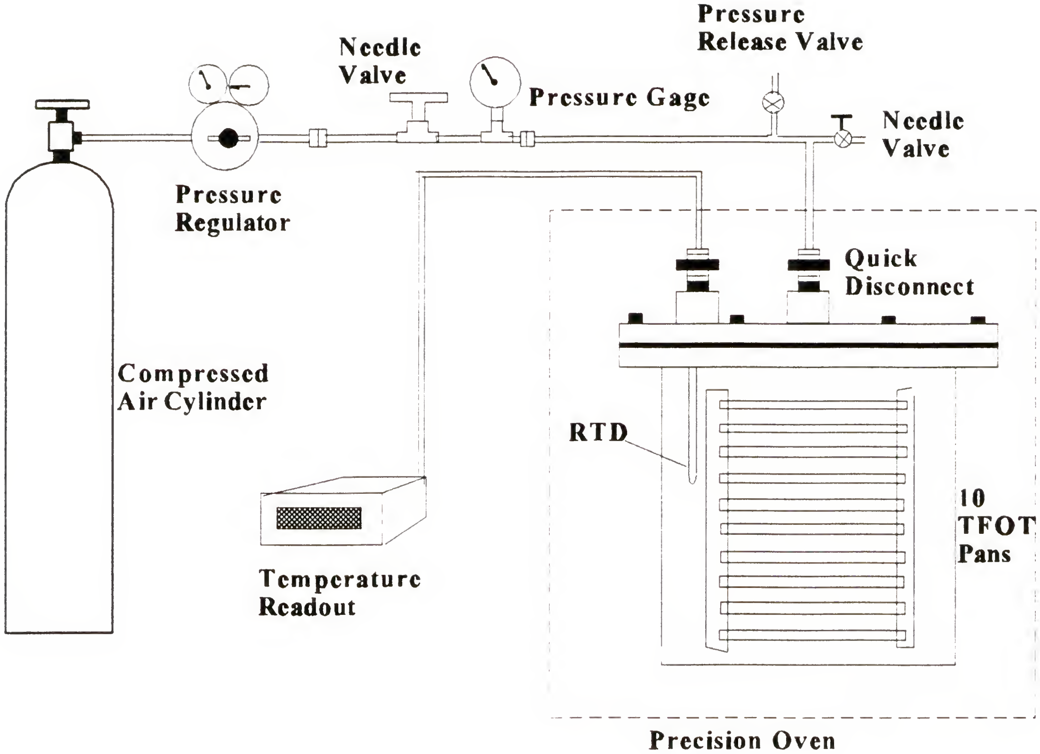


Figure 3-8 Schematic of PAV Test System

The new system uses SHRP modified vessel and a precision oven which were purchased by the Material Office of FDOT. The new system was performed following SHRP proposed procedure in accordances to AASHTO Designation PP1 [54, 57].

Both systems were performed under a pressure of 300 psi for 20 hours at three different temperatures of 90, 100, and 110 °C. In consideration of the convenience of the testing procedure in the old PAV system, it was decided to perform the PAV test on TFOT residues (50 g samples transferred directly from TFOT oven), rather than on RTFOT residues. A comparison of the differences between these two systems as well as a TFOT and a RTFOT treatment of the asphalt sample prior to the PAV process was also performed in this study.

3.4 Investigation on Aging of Asphalt Mixtures

In the investigation of asphalt aging in the mix, both loose mixtures and compacted samples were used. For each situation, the same aggregate and gradation were used to control the effect of the aggregate. Different laboratory aging processes nature aging under sunlight were evaluated. The main evaluation parameter is the viscosity of the recovered asphalt.

3.4.1 Aging of Asphalt Mixtures in the Laboratory

The testing program on the aging of asphalt mixture in the laboratory is shown in Figure 3-9. Florida S-I asphalt mixtures made with the five conventional asphalts used in this study were prepared in the laboratory. A portion of the loose asphalt mixtures were then aged in a forced-draft oven and a UV chamber at 60 °C for 28 days. The other mixtures were subjected to SHRP proposed aging procedures for asphalt mixtures [58].

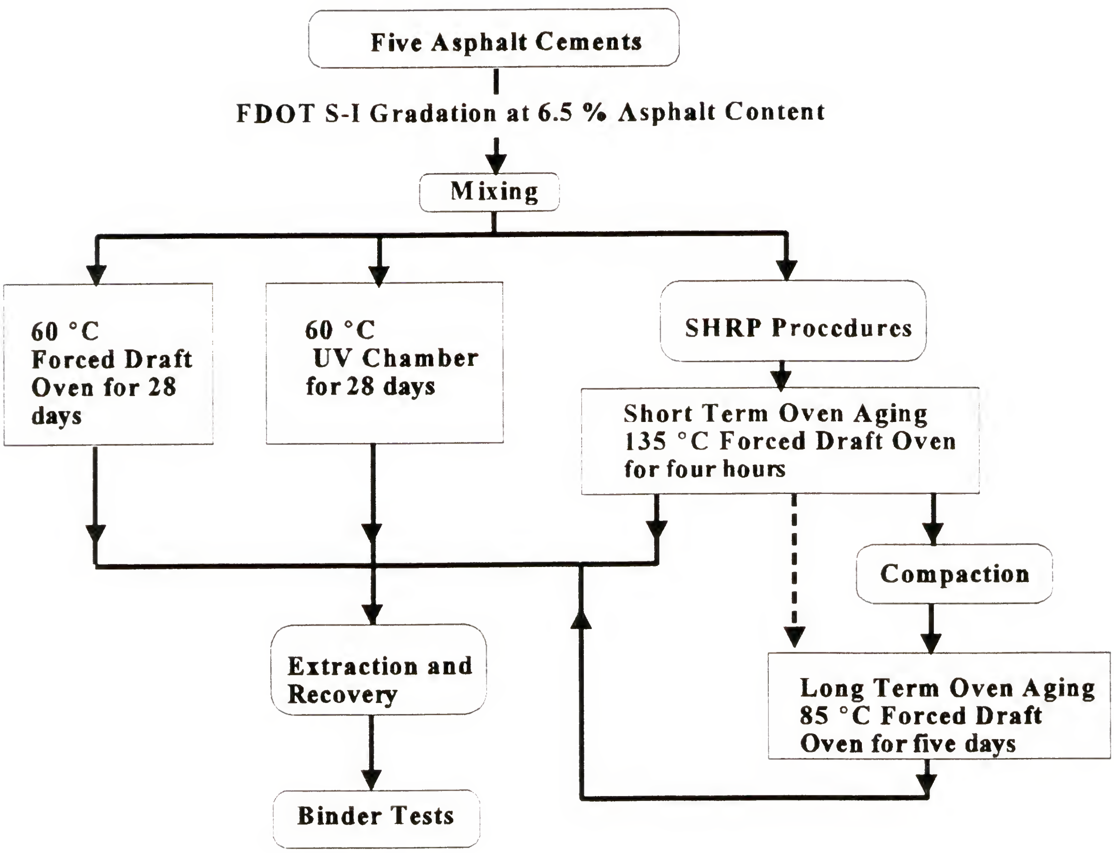


Figure 3-9 Testing Program for Asphalt Mixtures

Asphalt mixtures which were mixed in the laboratory were subjected, in there loose state, to short term oven aging (STOA) at 135 °C for four hours with mixing at each hour interval. After STOA, the mixtures were compacted by a 50-blow Marshall hammer and the compacted samples were subjected to an 85 °C forced draft oven for five days to simulate the long term oven aging (LTOA). Loose mixtures aged in the STOA were further aged in the LTOA for obtaining a more severe aging. Two replicate samples were tested per condition. This amounts to a total of ($5 \times 5 \times 2$ =) 50 samples to be tested in this substudy.

The same ultraviolet chamber used for binder aging was used for the aging of the loose mixtures. A conventional oven was modified to be a forced draft oven for this study as shown in Figure 3-10. A large inlet port was installed on one side and a small exit port on the top of the oven. These two ports were connected externally by a flexible aluminum duct. An air booster was used to circulate the air in the oven. The temperature was controlled by a thermostat switch and sensor. A Resistance Thermal Detector (RTD) was used to monitor the temperature.

3.4.2 Aging of Marshall Samples under Natural Sunlight

Marshall specimens which were fabricated in the previous study and aged under sunlight continued to be evaluated in this study. Five different types of AC-30 were used for making these samples [17]. FDOT S-I mixes with 6.5 % asphalt content were compacted by the 50-blow Marshall hammer to form Marshall samples with an average air void content of 5.0 %. Specimens which had reached ages of 2 and 4 years were evaluated. The aged binders were recovered and tested.

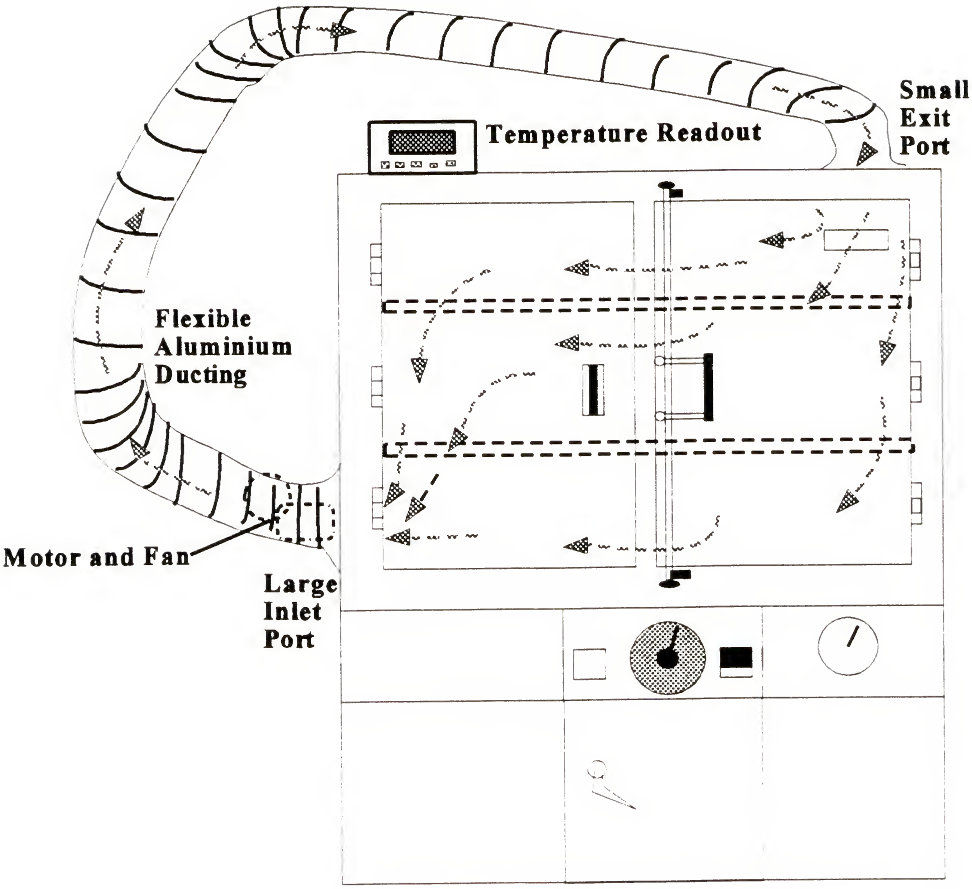


Figure 3-10 Schematics of Forced Draft Oven

3.5 Investigation on the Aging Characteristics of Modified Asphalt Binders

The aging characteristics of a few modified binders were investigated in this study. Figure 3-11 shows the testing program. Five modifiers, as listed earlier in Table 3-1, which include fine ground tire rubber (GTR), carbon black (CB), styrene ethylene butylene styrene (SEBS), ethylene vinyl acetate (EVA), and styrene butadiene rubber (SBR) were blended at adequate dosage levels with an AC-30 to produce five blends of modified AC-30 asphalts. These modified binders were subjected to the California Tilt Oven and Pressure Aging Vessel aging processes and their aged residues were tested for evaluating the effect of modifiers on the aging characteristics of asphalt binder.

3.6 Equipment for Binder Tests

The following binder tests were performed on the unaged and the aged samples:

(1) Penetration at 25 °C, ASTM D5.

(2) Absolute viscosity at 60 °C, ASTM D2171.

(3) Schweyer rheometer at 25 and 5 °C.

(4) Infrared absorption spectral analysis.

In the investigation on aging of asphalt mixtures, only the viscosity at 60 °C of the recovered residues was measured. A Brookfield Rheometer test was used to substitute for the absolute viscosity test in some cases. This section describes some special facilities for the binder tests used in this study including a Canon Schweyer Rheometer, a Brookfield Rheometer, and an Infrared Spectrophotometer.

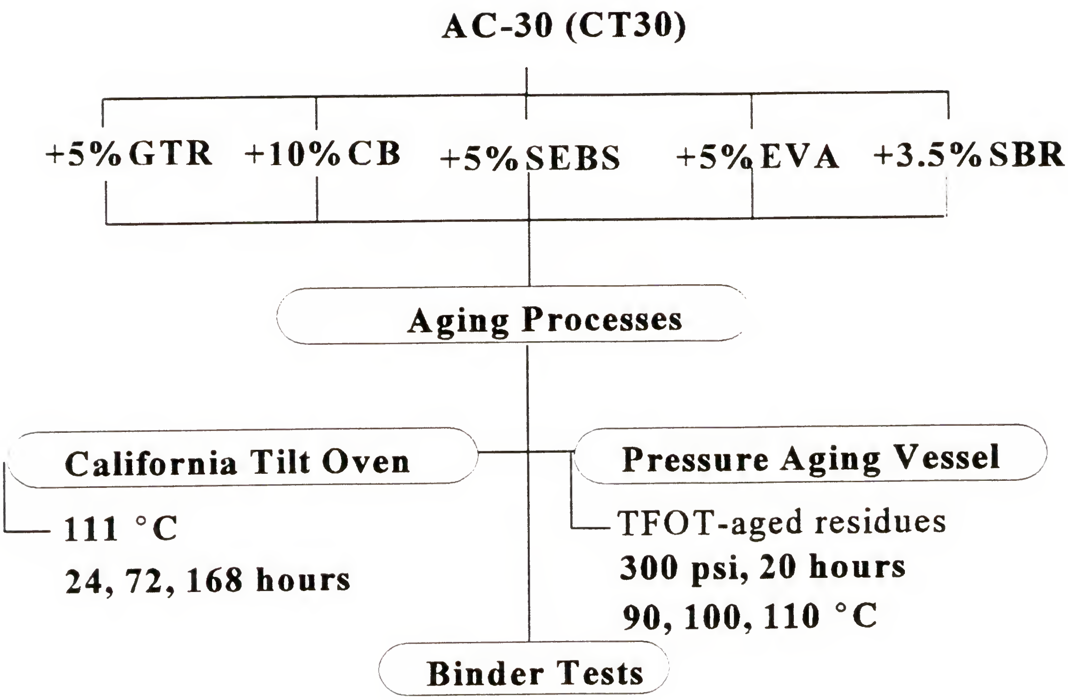


Figure 3-11 Testing Program on Aging Characteristics of Modified Asphalt Binders

3.6.1 Cannon Schweyer Constant Stress Rheometer

A Cannon Schweyer Constant Stress Rheometer as shown in Figure 3-12 and Figure 3-13 was used to characterize low temperature rheology of the binders in this study. A comprehensive review on the theoretical background for the Schweyer constant stress rheometer and the application of rheological concepts proposed by H. E. Schweyer has been presented in a paper by Tia and Ruth [32]. The rheometer consists of a gas-operated pneumatic cylinder which applied a specified force to the plunger in the sample tube, as shown in Figure 3-13. A LVDT measured the movement of the plunger and the output voltage was digitized and acquired by a data acquisition and analysis system, which was operated on an IBM PC-compatible computer. The sample tube is inserted into an insulated aluminum block which is maintained at the test temperature using coolant from a refrigeration unit in combination with an electrical wire heater, as shown in Figure 3-12.

Based on the steady-state laminar flow of power law fluid in the capillary tube, the shear stress and shear rate under the applied pressure can be obtained from the movement of the plunger and dimensions of the tube. Tests are usually conducted at a minimum of five stress levels. The shear susceptibility is computed and used to calculate the constant power viscosity at 100 W/m^3. This is the viscosity when the shear stress times the shear rate equals 100 W/m^3.

A typical plot of shear stresses and shear rates at different test temperatures as shown in Figure 3-14 demonstrates that the 100 W/m^3 constant power viscosity has to be extrapolated far from the observed data points. The variation of 100 W/m^3 constant power viscosity is enlarged by the variability of the shear susceptibility value. In order to

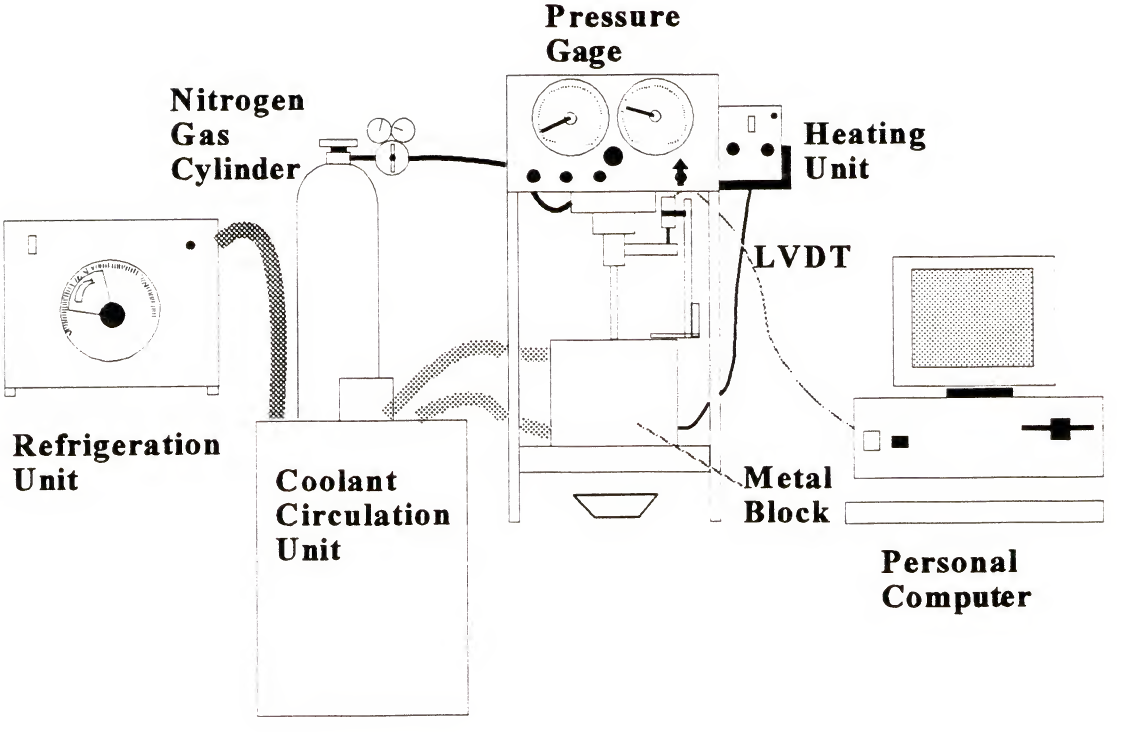


Figure 3-12 Canon Schweyer Rheometer System

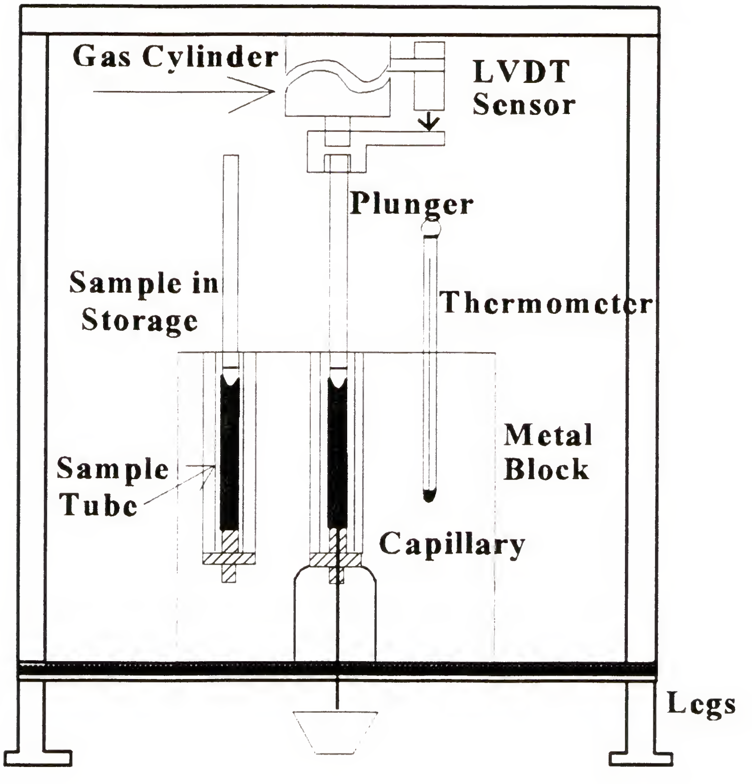


Figure 3-13 Schematic of Cannon Schweyer Rheometer

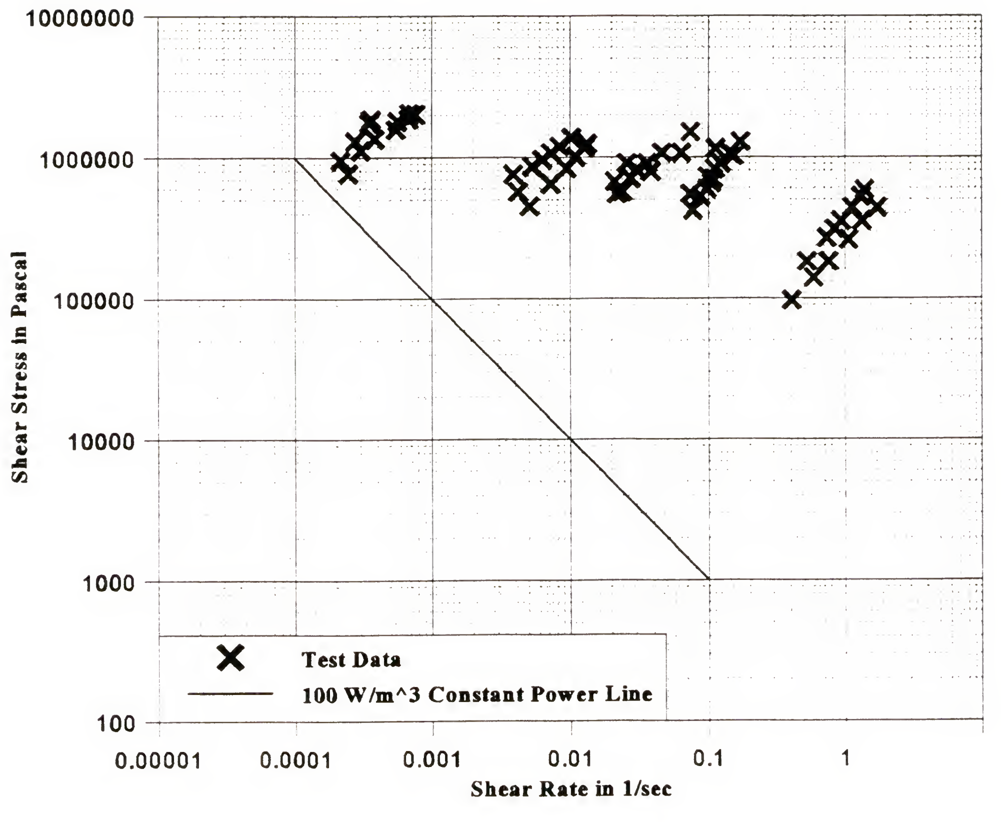


Figure 3-14 Shear Stresses and Shear Rates in Typical Schweyer Rheometer Tests

avoid the extrapolating error, an apparent viscosity at a shear stress of 1 MPa (Constant Stress Viscosity, CSV), which is close to the average shear stress used in performing the test, was used instead. This is the viscosity when the shear stress is at 1 MPa.

3.6.2 Brookfield Rheometer

A Brookfield Rheometer, model HB DV-3 with thermosel system, was used to replace the absolute viscosity test at 60 °C in the evaluation on aging of asphalt mixtures. The Brookfield Rheometer is a rotational viscometer. It measures the torque required to rotate an immersed element (the spindle) in a fluid. Figure 3-15 shows the schematic view of the major components of a Brookfield Rheometer [60]. The spindle of a known geometry (shearing area) is driven by a synchronous motor through a calibrated spiral spring. The deflection of the spring is indicated by the relative angular position of the pivot shaft which is detected by an RVDT (rotary variable displacement transducer).

The DV-3 model is designed to be connected to a personal computer to form a testing system as shown in Figure 3-16. A computer software developed by Brookfield Engineering Laboratories was used to read, store, and analyze data. Tests were performed at more than five rotation speeds (shear rates). A power law model (Equation 3) was used to analyze these data and the viscosity at shear rate equal to 1 1/sec, $\eta_{1.0}$ was selected to replace absolute viscosity. A total of 80 samples, which cover different types of modified binders and different degrees of age hardening, were tested for absolute viscosity and Brookfield viscosity at 60 °C. It can be observed in Figure 3-17 that $\eta_{1.0}$ is larger than the absolute viscosity obtained from capillary tube in the lower viscosity range ($\leq$ 10000 poises), while the reverse is true in the high viscosity range ($\geq$ 10000 poises). It

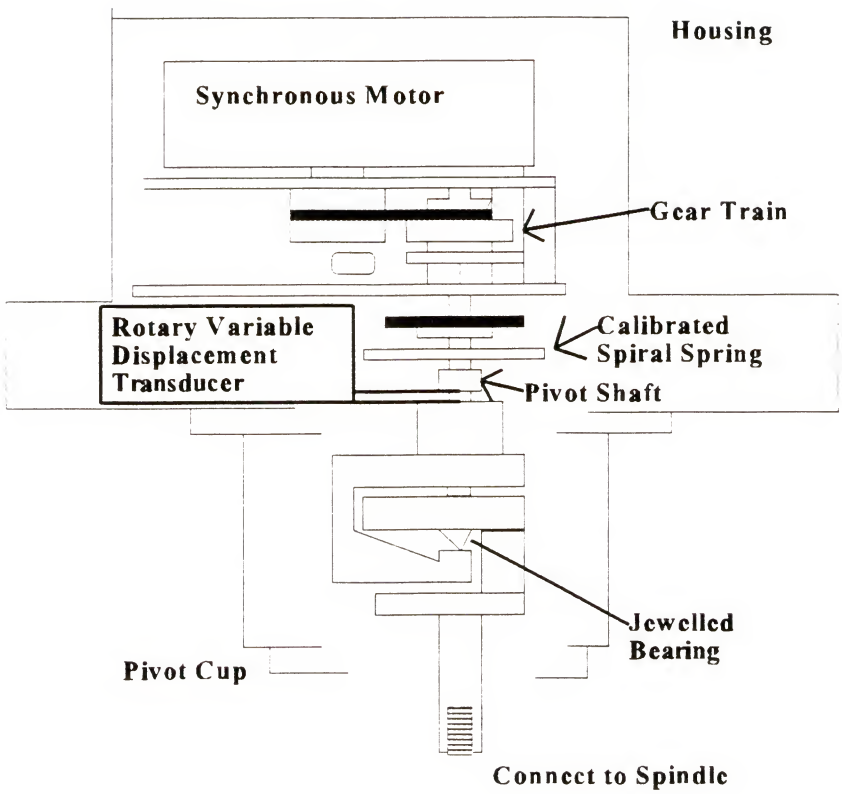


Figure 3-15 Schematics of the Major Components of a Brookfield Rheometer (Source: [60])

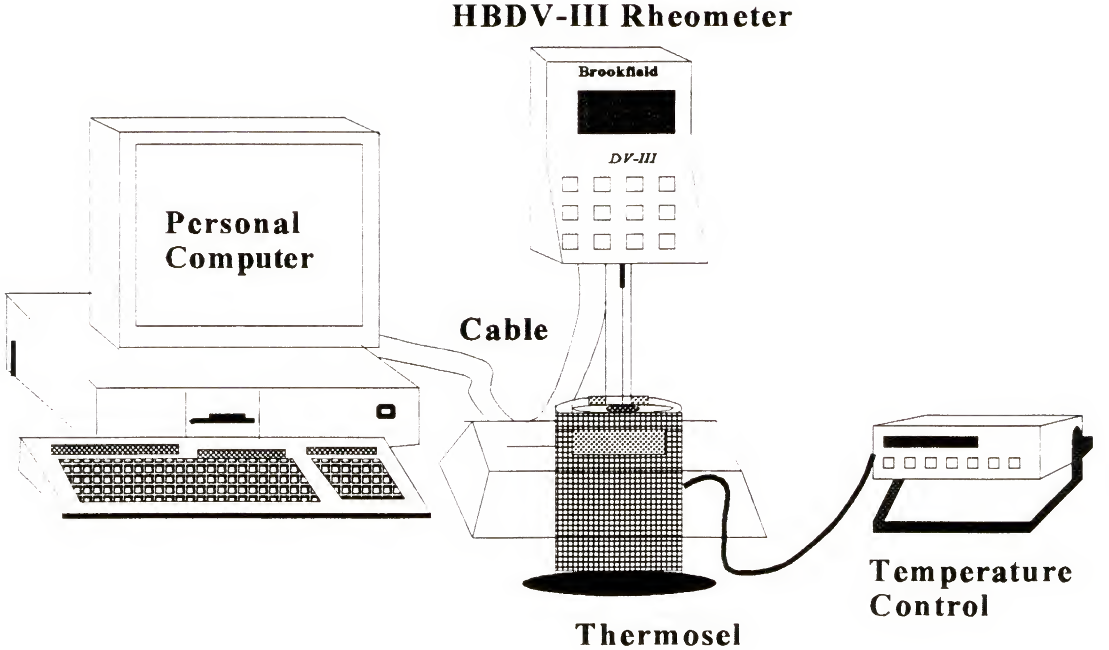


Figure 3-16 Brookfield HBDV-III Rheometer Reading and Controlling System

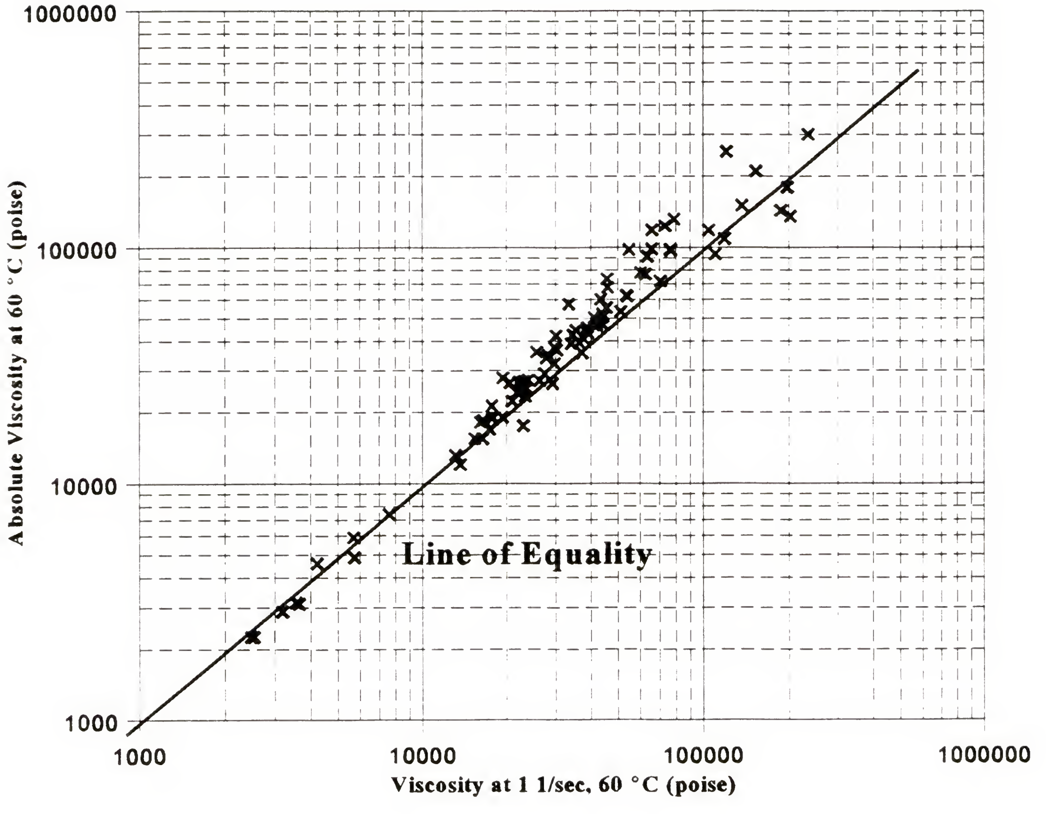


Figure 3-17 The Comparison of Brookfield Viscosity at Shear Rate of 1 sec^{-1} with Capillary Tube Viscosity at 60 °C

is believed that $\eta_{1.0}$ can be used in place of the absolute viscosity. To insure the consistency of data, a regression analysis was performed and a conversion equation was established to convert the Brookfield data to absolute viscosity.

3.6.3 Infrared Spectrophotometer

Figure 3-18 shows the Perkin-Elmer Model 1600 Fourier Transformation Infrared (FTIR) spectrophotometer used in this study. It consists of three major parts: an optical system, a sample compartment, and a dedicated computer. The computer controls the optical components, collects and stores data, performs computations on data and displays spectra.

The optical system illustrated in Figure 3-18 shows the optical path in the spectrophotometer [61]. The IR beam begins at the source coils. A fixed toroidal mirror collimate the beam from the source and directs it to the interferometer. The beam from a helium neon laser follows the IR beam through the interferometer. The system uses the laser beam to track the distance the moving mirror travels (optical path difference) and to determine when to take a data point.

The sample compartment is located at the front of the instrument, to the left of center. The single infrared beam enters the compartment from the left, behind the sample slide holder. After passing through the sample, it exits at the right, to enter the detector area. Liquid samples are examined for their spectral characteristics in sealed cells. These cells for handling solutions vary in thickness from 0.1 mm to 1.0 mm, the thickness representing the path length through the film of solution held between two crystal windows. The increase in path length results in higher absorbance values and a higher

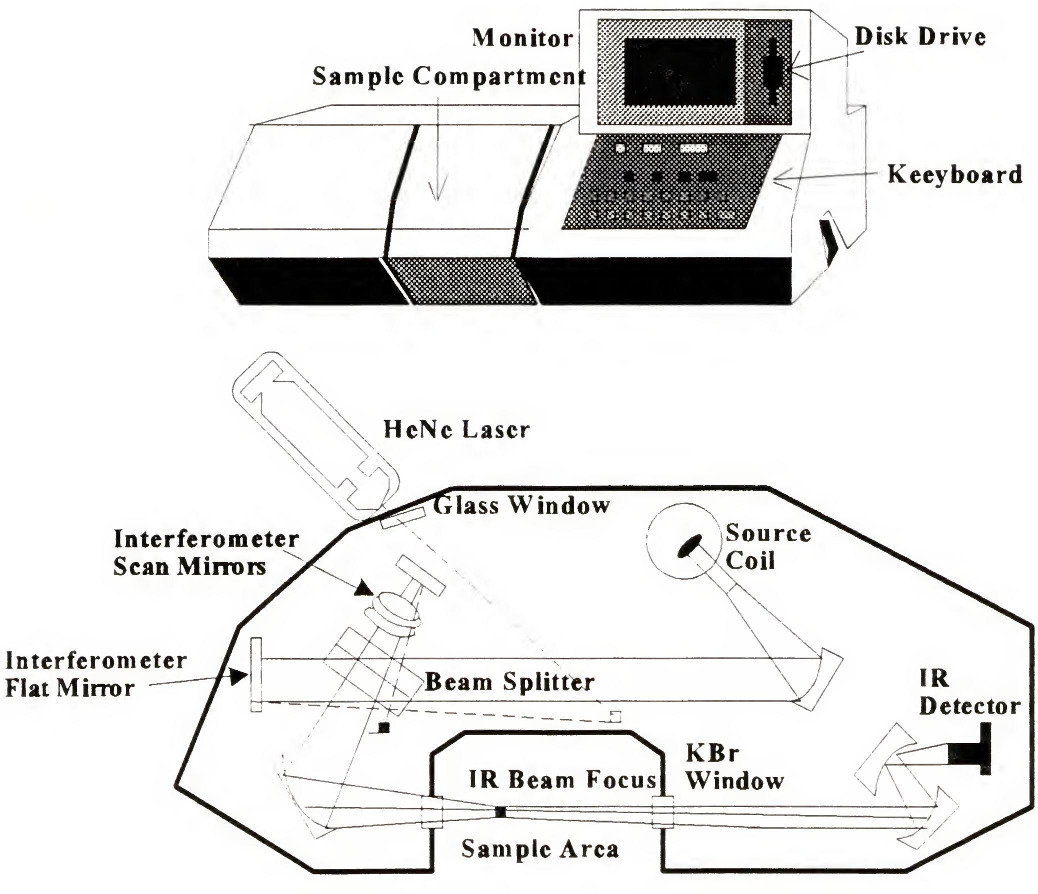


Figure 3-18 The Perkin-Elmer Model 1600 Spectrophotometer and its Optical System (Source: [61])

signal-to-noise ratio. The crystal windows are generally made of optical grade sodium chloride (NaCl) or potassium bromide (KBr). The Spectra Tech 1.0 mm NaCl sealed cells were used in the FTIR tests. Solutions of asphalt in tetrahydrofuran (THF) at 5 % (W/V) were injected (by using a syringe) into the cell for test.

3.7 Methodology for Analysis of Data

Results from this study were used to perform the correlation analysis as shown in Figure 3-19. The properties of the laboratory-aged binders were to be compared to those of the recovered binders from the laboratory-aged loose mixtures, the compacted Marshall specimens aged under natural sunlight, and core samples from paving projects. Whenever it is possible, the statistical tools such as Analysis of Variance was used. The aging indices based on viscosity measurements and carbonyl ratio index were used to perform analyses in the following main areas:

(1) The comparison between the aging effects on asphalt binders of the extended TFOT, UV chamber, California Tilt Oven and the Pressure Aging Vessel.

(2) The relative aging-severity between the aging of binders in loose mixtures and that of pure binders.

(3) The relative aging-severity between the aging of binders in loose mixtures and that of binders in Marshall samples aged under Florida climate.

(4) The comparison of aging of naturally aged Marshall samples with that of the asphalt mixtures in the field.

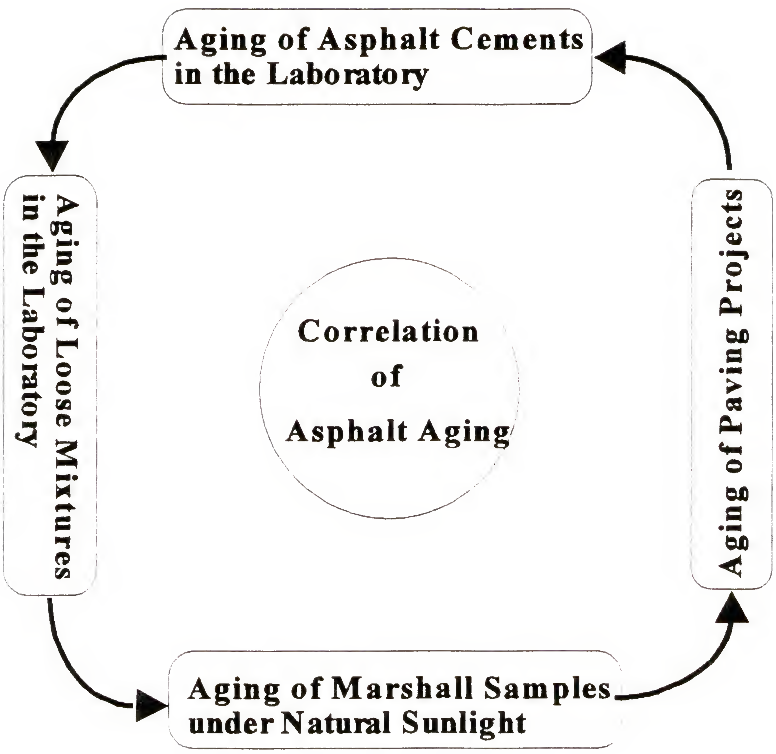


Figure 3-19 The Correlation of Test Data in this Study

CHAPTER 4
ASPHALT EXTRACTION AND RECOVERY METHOD

4.1 Sampling and Testing

A testing program was performed to investigate the difference between the different asphalt extraction and recovery methods, and to determine the most effective procedure to be used by the FDOT. An FDOT S-III mixture (original, no recycled materials) was obtained from a truck load at a local asphalt batch plant. The acquired mixture was randomly separated and stored in 36 sealed aluminum pans, each sample weighing 1300 g, which is the approximate amount for a Marshall sample. Asphalts were extracted from these samples using three different extraction and three recovered methods as described in section 3.2.

For the analysis of data, a 3^2 complete factorial experiment was conducted using four replicate samples per extraction/recovery combination. The following linear model is assumed for any single observation in the experiment:

$$y_{ijk} = \mu + \tau_i + \beta_k + \tau\beta_{ij} + \epsilon_{ijk} \qquad (11)$$

Where :

y_{ijk} = the k^{th} observation on the i^{th} extraction (τ), j^{th} recovery (β).

μ= overall mean of all observations.

τ_i= the main effect of i^{th} extraction method.

β_j= the main effect of j^{th} recovery method.

$\tau\beta_{ij}$= two-factor interaction effects.

ϵ_{ijk}= random errors.

i= 1 ~ 3, for three different extraction methods.

j= 1 ~ 3, for three different recovery methods.

k= 1 ~ 4, for four replicates.

4.2 Test Results

The results of penetration and absolute viscosity tests on the recovered binders are shown in Table 4-1. Among the three different extraction procedures, the reflux method produces the lowest average standard deviation, and so does the Abson method among the three recovery procedures. This is due to the fact that reflux/Abson procedure is the routine method used by FDOT and the test personnel are familiar with this procedure. The only hot extraction method, the reflux, seems not to have particular hardening effect in comparison to the other two cold extraction methods.

The results of ANOVA and Duncan's multiple range test on the absolute viscosity and penetration data are shown in Table 4-2 and Table 4-3 respectively. It can be seen that the effects of different extraction methods on the penetration data are significant. The centrifuge extraction results in significantly lower penetration values than those from the reflux and vacuum extraction. However, the effect of extraction methods is not significant when the absolute viscosity was used as the evaluation parameter.

The effects of different recovery methods, however, are significant not only on the penetration but also on the viscosity values. Rotovapor 2 tends to result in a higher

Table 4-1 Absolute Viscosities and Penetrations of the Asphalts Recovered by the Different Combinations of Method

	No.	Reflux	Centrifuge	Vacuum	Average
Abson	1 2 3 4	5321@(51#) 5949(47) 5499(48) 5470(49)	6981(42) 5981(43) 6667(42) 7531(40)	5731(46) 6447(43) 6013(44) 6407(43)	
	Average	5560(48.8)	6790(41.8)	6150(44.0)	6167(44.9)
	STD*	271(1.7)	647(1.3)	341(1.4)	420(1.5)
Rotovapor 1	1 2 3 4	3947(68) 3478(67) 4441(56) 3972(62)	4561(55) 4707(54) 4690(56) 4959(53)	2599(78) 3768(66) 4001(62) 5738(50)	
	Average	3960(63.2)	4729(54.5)	4026(64.0)	4238(60.6)
	STD	393(5.5)	166(1.3)	1295(11.5)	618(6.1)
Rotovapor 2	1 2 3 4	6933(40) 6943(41) 6924(40) 6538(40)	7539(37) 7373(39) 6675(40) 7109(39)	5731(47) 6164(44) 8726(44) 9093(41)	
	Average	6834(40.2)	7174(38.8)	7428(43.2)	7145(40.7)
	STD	198(0.5)	377(1.2)	1725(2.9)	767(1.5)
	Average	5451(50.7)	6231(45.0)	5868(50.4)	5850(48.7)

Note:

@ Absolute viscosity at 60 °C in poises.
# Penetration at 25 °C in 1/100 cm.
* Standard deviation.

Table 4-2 Results of ANOVA and Duncan's Multiple Range Test on Penetration Data

Source	DF	Mean Square	F Value	Pr > F
EXTRACTION, τ_i	2	125.027778	6.19	0.0061
RECOVERY, β_j	2	1316.194444	65.15	0.0001
INTERACTION, $\tau\beta_{ij}$	4	29.319444	1.45	0.2445
Error	27	20.203704		

R-Square: 0.846131

Duncan Grouping	Mean	N	EXTRACTION
A	50.750	12	Reflux
A			
A	50.417	12	Vacuum
B	45.000	12	Centrifuge

Duncan Grouping	Mean	N	RECOVERY
A	60.583	12	Rotovapor 1
B	44.833	12	Abson
C	40.750	12	Rotovapor 2

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.

Table 4-3 Results of ANOVA and Duncan's Test on Absolute Viscosity Data

Source	DF	Mean Square	F Value	Pr > F
EXTRACTION, τ_i	2	1827336.08	2.92	0.0710
RECOVERY, β_j	2	26256434.25	41.99	0.0001
INTERACTION, $\tau\beta_{ij}$	4	387461.46	0.62	0.6553
Error	27	625318.17		

R-Square: 0.773649

Duncan Grouping		Mean	N	EXTRACTION
	A	6231.1	12	Centrifuge
	A			
B	A	5868.2	12	Vacuum
B				
B		5451.3	12	Reflux

Duncan Grouping	Mean	N	RECOVERY
A	7145.7	12	Rotovapor 2
B	6166.4	12	Abson
C	4238.4	12	Rotovapor1

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.

viscosity and a lower penetration value, while rotovapor 1 tends to produce the opposite results. The lower viscosity value obtained from the rotavapor 1 was caused possibly by the fact that some of the solvent had not been completely driven out of the binders, due to the absence of the nitrogen purge. It is very likely that the purge-in of nitrogen (or CO_2) which is used in the Abson and rotavapor 2 procedures help drive out the vapor of the solvent.

4.3 Summary of Findings

To be used as a routine test, the extraction/recovery procedure has to be easy to run. The centrifuge and vacuum extraction methods produced an average volume of solution of about 800 ml as compared with about 400 ml for the reflux procedure. As compared with an average process time of one hour for the rotavapor methods, the Abson recovery method takes one more hour to run on the larger volume of solutions produced by the centrifuge or vacuum extraction. The rotavapor recovery method can accommodate larger solution volume, which is more desirable in routine tests.

The following conclusions were derived from this substudy.

(1) The reflux extraction method, which is used in FDOT's routine work, does not appear to cause a greater hardening effect on the extracted binders as compared with the other two cold extraction methods when the absolute viscosities of the recovered binders are considered.

(2) The effects of the different extraction methods on the absolute viscosities of recovered asphalts are not significantly different from one another.

(3) Different recovery methods are very likely to produce different results. The use of a nitrogen (or carbon dioxide) purge in the Abson or Rotavapor procedure was found to be effective in driving out the solvent from the recovered binders completely.

(4) The reflux/Abson method, which was used in FDOT's routine work, appears to be adequate as long as test personnel have been trained to control the temperature in the Abson procedure.

(5) The combination of rotavapor with reflux, which has been adopted by FDOT recently, is the most effective procedure. However, a possible increase in the viscosity of recovered binders might be noticed.

CHAPTER 5
COMPARISON OF DIFFERENT AGING METHODS ON ASPHALT BINDERS

5.1 Introduction

In the investigation of different aging methods on conventional asphalt cements, a total of 17 levels of aging were applied on five asphalts. For comparing the aging severity of different aging methods, different parameters such as the aging indices based on the viscosity measurements, and the carbonyl ratio index based on the infrared spectral analysis, were used. An appropriate statistical model was used to analyze the data and compare the aging severities of different aging procedures. The conventional temperature susceptibility parameters including *PI*, *PVN*, and β_1 were used to evaluate the effects of aging on the temperature susceptibility of the asphalt binders.

5.2 Statistical Model

In the comparison of different aging processes, the test results were analyzed as a 5×17 factorial experiment comprising of five asphalts (τ), and 17 aging methods (β). In the study, the concern is on the specified 17 aging processes and five asphalts. Therefore, τ and β are regarded as fixed effects. The following linear model is assumed for any single response in the experiment:

$$Y_{ijk} = \mu + \tau_i + \beta_j + \tau\beta_{ij} + \epsilon_{ijk} \qquad (12)$$

Where

Y_{ijk} = the response of k^{th} replicate, j^{th} aging method, and i^{th} asphalt.

μ = the overall mean.

τ_i = the main effect of i^{th} asphalt.

β_j = the main effect of j^{th} aging method.

$\tau\beta_{ij}$= the interaction effect.

ϵ_{ijk}= the experimental error.

i = 1 to 5 for five asphalts.

j = 1 to 17 for the 17 different aging methods.

k = 1 to 2 for two replicates.

The adequacy of the model depends on the assumption that the errors (ϵ_{ijk}) are normally and independently distributed with mean zero and constant variance σ^2. The Burr-Foster Q-Test of homogeneity [62] were performed on the aging index at 60 °C in both untransformed and the logarithm-transformed data. The hypothesis of homogeneity were rejected in both cases indicating the inequality of variances when the aging index is used as the response.

According to Lyman Ott [63] and Ruppert G. Miller [64], the effect of unequal variances on the F-test can be serious but is less so in the case of equal sample sizes. In the latter case, the true p-values for the F-test in the analysis of variance table will be only mildly distorted. Thus, although the assumption of equal variances was not satisfied and the results of ANOVA may be unreliable, it was decided to perform the ANOVA on the logarithm-transformed data in order to identify the main effects of viscosity.

5.3 Test Results

The test data of penetration, carbonyl ratio, absolute viscosity at 60 °C, constant stress (1MPa) viscosity at 25 °C, and constant stress (1MPa) viscosity at 5 °C are listed in Table A-1 through Table A-5, respectively, in Appendix A. These results were analyzed by using the statistical model as described in the previous section. The percent penetration retained, the carbonyl ratio index, and the logarithm of aging indices at three different temperatures were used as the response variables in Equation 12. Different evaluation parameters were analyzed separately. The weight of the samples were measured in some aging processes before and after aging and the data are included in this section.

5.3.1 Weight Change

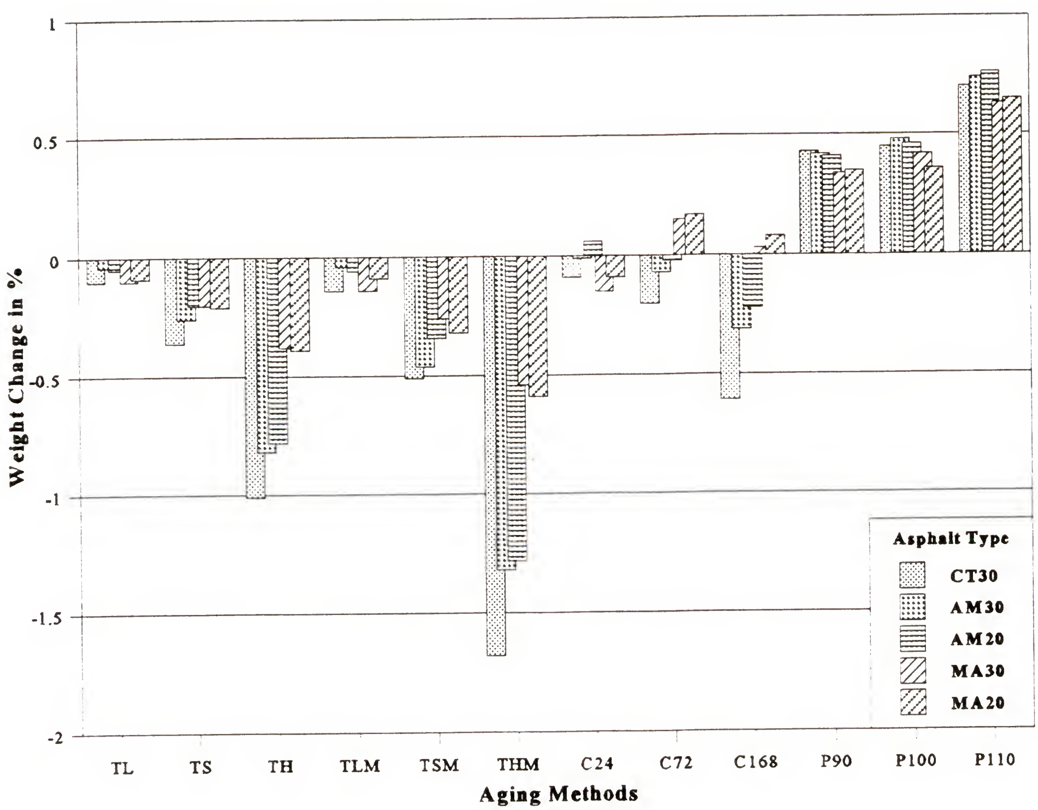
Table 5-1 lists the weight change of the five asphalts after the processes of extended TFOT, CTO, and PAV. These three groups of aging methods show three different weight change patterns as shown in Figure 5-1. The weight changes after the processes of TFOTs and CTOs are differentiable by refinery source of asphalt. CT30 shows the highest weight loss, and the AM asphalts show higher weight loss than the MA asphalts. MA asphalt, which has the least weight loss in the TFOTs, exhibited weight gain in the CTO processes. Among the 17 aging processes, the high temperature TFOT (using 50 g or 25 g samples) produced substantially large amounts of weight loss with the highest value of 1.68 %. On the other hand, the SHRP proposed PAV processes produce substantially large amount of weight gain as shown in Figure 5-1 with the highest value of 0.76 %. However the PAV-aged residues are not differentiable by refinery source in

Table 5-1 Weight Change of Different Asphalt Cements after the Process of TFOT, CTO, and PAV

Laboratory Aging Process	Change of Weight in %				
	CT30	AM30	AM20	MA30	MA20
TL	- 0.10	- 0.04	- 0.05	- 0.10	- 0.09
TS	- 0.36	- 0.26	- 0.20	- 0.20	- 0.21
TH	- 1.01	- 0.82	- 0.78	- 0.38	- 0.39
TLM	- 0.14	- 0.04	- 0.06	- 0.14	- 0.09
TSM	- 0.51	- 0.46	- 0.34	- 0.26	- 0.32
THM	- 1.68	- 1.32	- 1.28	- 0.54	- 0.59
C24	- 0.09	- 0.01	0.06	- 0.15	- 0.09
C72	- 0.20	- 0.07	- 0.02	0.15	0.17
C168	- 0.61	- 0.31	- 0.22	0.03	0.08
P90	0.43	0.42	0.41	0.34	0.35
P100	0.45	0.48	0.46	0.42	0.36
P110	0.70	0.74	0.76	0.63	0.65

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.



Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Figure 5-1 Weight Change of Five Asphalts after Different Aging Methods

terms of weight change. The difference in the effect of refinery source seems to be enlarged by using a higher exposure temperature in the TFOT and PAV processes.

5.3.2 Penetration

The penetration data, as listed in Table A-1, are used for comparing the aging severity in terms of percent penetration retained as determined according to Equation 1. Table 5-2 lists the percent penetration retained for the five asphalts at the 17 aging levels. These data are plotted in Figure 5-2. As shown in Figure 5-2, the most severe aging process was found to be the California Tilt Oven for 168 hours (C168). The residues of all five asphalts exhibit a penetration value less than 20 in the process of C168 as listed in Table A-1. The modified TFOT processes (using 25 g sample) produce a much lower percentage of penetration retained as shown in Figure 5-2. The three aging levels of UV Chamber produced similar aging severity in terms of percent penetration retained. The PAV processes harden the asphalts to approximately 40 % of penetration retained.

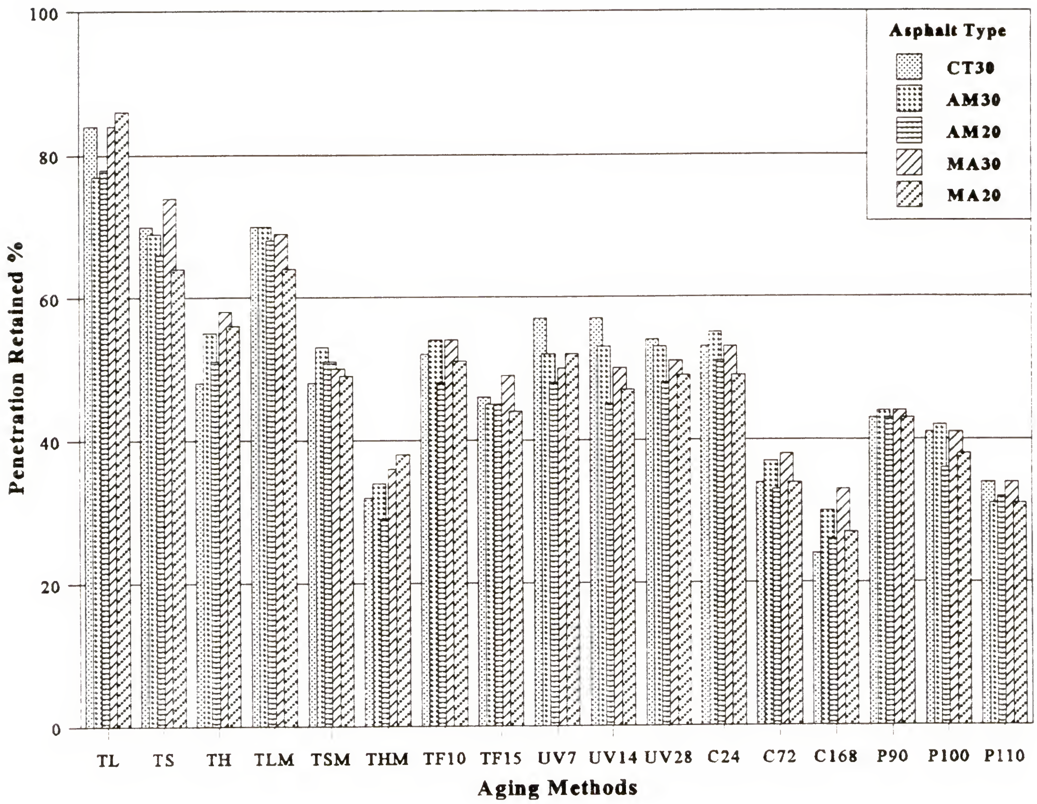
The results of ANOVA on the percent penetration retained, which are displayed in Table 5-3, show that the five asphalts have different age hardening characteristics and there is no significant interaction effect between asphalt type and aging methods. The Duncan's Multiple Range test was performed to compare the means of different asphalts and different aging methods with a probability of Type I error of 0.05 (α=0.05). The results of the Duncan's tests are also shown in Table 5-3. The asphalts and methods which are denoted by the same letters are not significantly different from one another. It can be seen that the percent penetration retained of AC-30s are significantly higher than those of AC-20s. However the percent penetration retained is independent of the refinery source.

Table 5-2 Percent Penetration Retained of Residues of five Asphalts at Different Aging Conditions

Laboratory Aging Process	Penetration Retained in % (Average of two replicates)				
	CT30	AM30	AM20	MA30	MA20
TL	84	77	78	84	86
TS	70	69	66	74	64
TH	48	55	51	58	56
TLM	70	70	68	69	64
TSM	48	53	51	50	49
THM	32	34	29	36	38
TF10	52	54	48	54	51
TF15	46	45	45	49	44
UV7	57	52	48	50	52
UV14	57	53	45	50	47
UV28	54	53	48	51	49
C24	53	55	51	53	49
C72	34	37	33	38	34
C168	24	30	26	33	27
P90	43	44	43	44	43
P100	41	42	36	41	38
P110	34	31	32	34	31

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.



Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Figure 5-2 Percent Penetration Retained of Five Asphalts Aged by the 17 Aging Methods

Table 5-3 Results of ANOVA and Duncan's Multiple Range Test on the Percent Penetration Retained in the Comparison of Different Aging Methods on Asphalt Cements

Dependent Variable: % penetration retained

Source	DF	Sum of Squares	Mean Squares	F Value	Pr > F
Model	84	33415.49082	397.80346	20.02	0.0001
Error	85	1688.83420	19.86864		
Corrected Total	169	35104.32502			

R-Square	C.V.	Root MSE	Overall Mean
0.951891	9.009738	4.457425	49.4734118

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Asphalt (τ)	4	354.73976	88.68494	4.46	0.0025
Method (β)	16	32296.71262	2018.54454	101.59	0.0001
Interaction ($\tau\beta$)	64	764.03844	11.93810	0.60	0.9831

Duncan Grouping		Mean	N	Asphalt
	A	51.204	34	MA30
	A			
B	A	50.411	34	AM30
B	A			
B	A	50.138	34	CT30
B				
B	C	48.338	34	MA20
	C			
	C	47.276	34	AM20

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

Table 5-3 Continued

Duncan Grouping		Mean	N	Method
	A	82.680	10	TL
	B	68.674	10	TS
	B			
	B	68.611	10	TLM
	C	54.104	10	TH
	C			
D	C	52.800	10	UV7
D	C			
D	C	52.620	10	UV14
D	C			
D	C	52.328	10	C24
D	C			
D	C	51.270	10	TF10
D	C			
D	C	50.314	10	TSM
D				
D	E	49.100	10	UV28
	E			
F	E	45.480	10	TF15
F				
F		43.680	10	P90
	G	39.580	10	P100
	H	35.461	10	C72
	H			
	H	33.871	10	THM
	H			
	H	32.500	10	P110
	I	27.975	10	C168

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

When different aging methods are compared, the most severe aging process is the California Tilt Oven for 168 hours producing an average penetration retained of 28 %, which is significantly lower than those produced by the other methods. The PAV at 110 °C, high temperature (185 °C) TFOT using 25 g samples, and California Tilt Oven for 72 hours produce similar aging effect with an average penetration retained of 34 %. The PAV at 90 °C and TFOT for 15 hours produce a similar percentage of penetration retained. Due to the insensitivity of penetration measurements at lower penetration level, the percent penetration retained may be an inappropriate parameter for comparing the aging severity of harder asphalts.

5.3.3 Carbonyl Ratio

The results of Infrared Spectral analysis in terms of carbonyl ratio are displayed in Table A-2. The carbonyl ratio index, which is the ratio of carbonyl ratio of the aged residue to the carbonyl ratio of original asphalt, was used to describe the aging severity. A higher value of carbonyl ratio index means a more severe aging. The carbonyl ratio index of the residues of the five asphalts aged by the 17 aging processes are listed in Table 5-4 and plotted in Figure 5-3. The highest carbonyl ratio index was found to be 2.25 of MA20 residue aged by the CTO for 168 hours as shown in Figure 5-3.

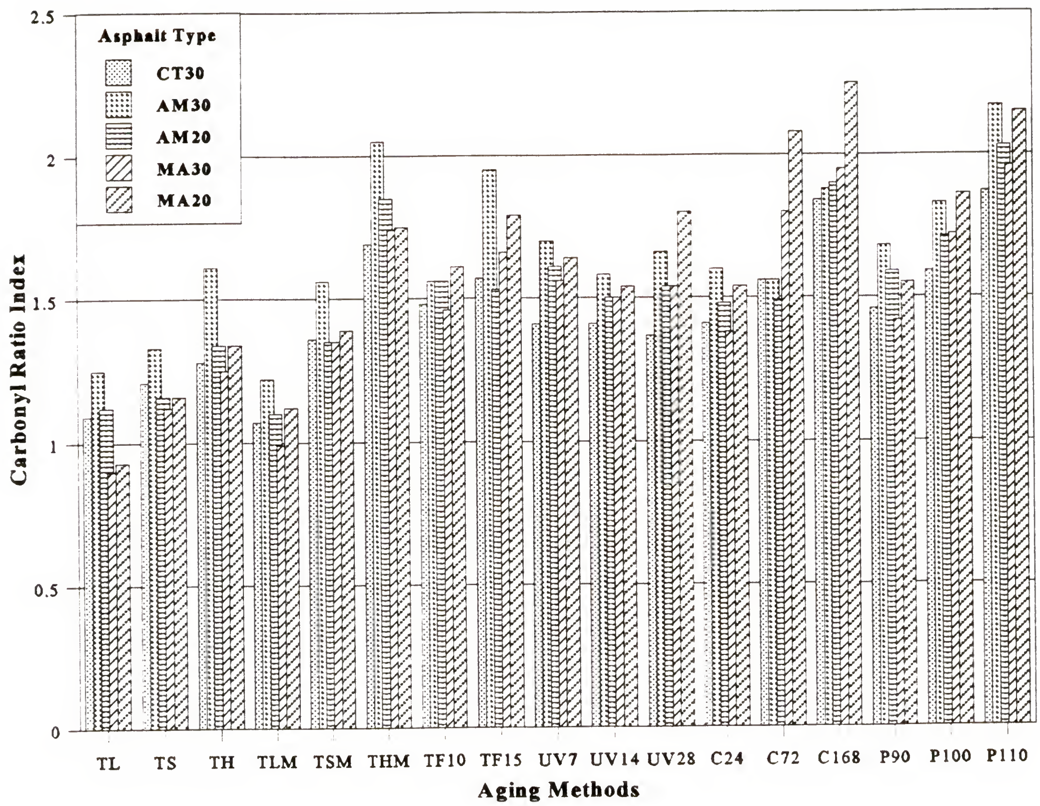
The results of ANOVA and Duncan's Multiple Range test are shown in Table 5-5. Both the effect of asphalt (τ) and mrthod (β) are significant and that of the interaction ($\tau\beta$) is not significant. These results are similar to the results of ANOVA on the percent penetration retained. The R-Square, however, is lower than that for percent penetration retained.

Table 5-4 Carbonyl Ratio Index of Residues of the Five Asphalts after the 17 Aging Processes

Laboratory Aging Process	Carbonyl Ratio Index				
	CT30	AM30	AM20	MA30	MA20
TL	1.09	1.25	1.12	0.90	0.93
TS	1.21	1.33	1.16	1.12	1.16
TH	1.28	1.61	1.34	1.25	1.34
TLM	1.07	1.22	1.10	0.99	1.12
TSM	1.36	1.56	1.35	1.35	1.39
THM	1.69	2.05	1.85	1.74	1.75
TF10	1.48	1.56	1.56	1.46	1.61
TF15	1.57	1.95	1.53	1.66	1.79
UV7	1.41	1.70	1.61	1.56	1.64
UV14	1.41	1.58	1.50	1.50	1.54
UV28	1.37	1.66	1.54	1.54	1.80
C24	1.41	1.60	1.48	1.38	1.54
C72	1.56	1.56	1.49	1.80	2.08
C168	1.84	1.88	1.90	1.95	2.25
P90	1.46	1.68	1.59	1.42	1.55
P100	1.59	1.83	1.71	1.72	1.86
P110	1.87	2.17	2.03	1.96	2.15

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.



Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Figure 5-3 The Carbonyl Ratio Index of the Residues of the Five Asphalts Aged by the 17 Aging Methods

Table 5-5 Results of ANOVA and Duncan's Multiple Range Test on the Carbonyl Ratio Index in the Comparison of Different Aging Methods on Asphalt Cements

Dependent Variable: Carbonyl Ratio Index

Source	DF	Sum of Squares	Mean Squares	F Value	Pr > F
Model	84	14.60644471	0.17388625	5.08	0.0001
Error	85	2.90960000	0.03423059		
Corrected Total	169	17.51604471			

R-Square	C.V.	Root MSE	Overall Mean
0.833889	11.91475	0.185015	1.55282353

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Asphalt (τ)	4	1.20753882	0.30188471	8.82	0.0001
Method (β)	16	12.04830471	0.75301904	22.00	0.0001
Interaction ($\tau\beta$)	64	1.35060118	0.02110314	0.60	0.9781

Duncan Grouping	Mean	N	Asphalt
A	1.6815	34	AM30
A			
A	1.6168	34	MA20
B	1.5235	34	AM20
B			
B	1.4897	34	MA30
B			
B	1.4526	34	CT30

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

Table 5-5 Continued

Duncan Grouping			Mean	N	Method
	A		2.0360	10	P110
	A				
B	A		1.9690	10	C168
B					
B	C		1.8430	10	THM
	C				
D	C		1.7430	10	P100
D	C				
D	C	E	1.7180	10	C72
D	C	E			
D	C	E	1.6970	10	TF15
D		E			
D	F	E	1.5840	10	UV7
D	F	E			
D	F	E	1.5840	10	UV28
	F	E			
G	F	E	1.5390	10	P90
G	F	E			
G	F	E	1.5330	10	TF10
G	F				
G	F		1.5050	10	UV14
G	F				
G	F		1.4970	10	C24
G	F				
G	F		1.4120	10	TSM
G					
G			1.3730	10	TH
	H		1.2080	10	TS
	H				
	H		1.0980	10	TLM
	H				
	H		1.0590	10	TL

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

It was found that the PAV at 110 °C generally produces a higher carbonyl ratio index than does the CTO for 168 hours, although the difference is statistically insignificant. The aging severity of the 17 aging processes, based on the carbonyl ratio index, is in a general agreement with that based on the percent penetration retained. The PAV at 100 °C produced a carbonyl ratio index of about 1.7, which is similar to those aged by CTO for 72 hours, TFOT at high temperature, and TFOT for 15 hours. The aging effects of three levels of UV chamber again are not significantly different in terms of carbonyl ratio index and are close to those aged by CTO for 24 hours, PAV at 90 °C, and TFOT for 10 hours. High temperature TFOT (THM) using 25-g samples was ranked relatively higher in aging severity in terms of carbonyl ratio index. This may indicate that high oxidation rate as well as the high loss of volatiles occurred in this process.

5.3.4 Absolute Viscosity

Table A-3 lists the absolute viscosity data. The aging index (viscosity ratio), as calculated by Equation 2, was used to represent the aging severity and the response in the statistical model. Table 5-6 shows the aging index at 60 °C based on the absolute viscosity data. The 17 aging methods produced a wide range of aging index at 60 °C, from 1.4 to a high value of 46 as shown in Figure 5-4.

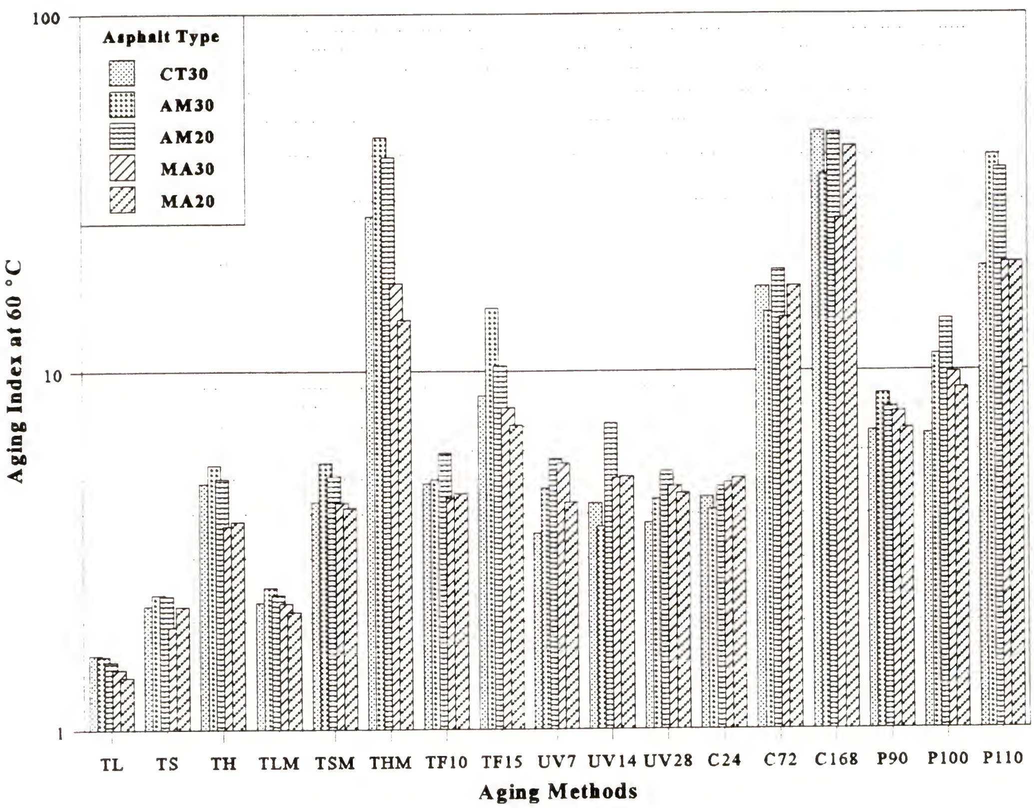
It is noticed that the asphalts (MA) with low volatile loss did show a lower aging index than the asphalts (AM) with higher volatile loss. However, CT30, which produced the highest weight loss in the extended TFOT, exhibits lower aging indices than the AM asphalts. The volatile loss does not seem to dominate the age hardening of asphalts in the process of TFOT at higher temperature.

Table 5-6 Aging Index at 60 °C of Residues of the Five Asphalts aged by the 17 Aging Processes

Laboratory Aging Process	Aging Index at 60 °C				
	CT30	AM30	AM20	MA30	MA20
TL	1.61	1.60	1.55	1.47	1.40
TS	2.21	2.37	2.35	1.93	2.20
TH	4.87	5.47	5.00	3.68	3.80
TLM	2.26	2.49	2.37	2.25	2.13
TSM	4.31	5.55	5.10	4.28	4.14
THM	27.08	44.98	39.45	17.63	13.94
TF10	4.84	4.96	5.90	4.41	4.55
TF15	8.54	15.01	10.37	7.91	7.08
UV7	3.52	4.71	5.68	5.52	4.29
UV14	4.27	3.67	7.16	5.03	5.08
UV28	3.77	4.38	5.24	4.76	4.54
C24	4.23	4.09	4.75	4.86	5.00
C72	16.39	14.59	19.16	14.11	17.24
C168	44.31	35.31	46.13	26.61	42.30
P90	6.48	8.64	7.90	7.70	6.90
P100	6.35	11.12	13.97	9.88	8.94
P110	18.65	39.75	36.68	20.02	20.04

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.



Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Figure 5-4 Aging Index at 60 °C of the Residues of the Five Asphalts Aged by the 17 Aging Methods

A close examination of the aging indices at 60 °C of different asphalts after the processes of the UV Chamber as shown in Table 5-6 reveals that there was no significant additional hardening of the asphalt residues from 7 days to 28 days exposure in the UV chamber. This might be due to the formation of a thin skin on the surface of the asphalt residue during early UV exposure, which might seal the rest of the asphalt residue from further oxidation.

In the California Tilt Oven processes, AC-20s show higher aging indices than AC-30s. This might be due to the higher mobility of the less viscous AC-20, resulting in a larger exposure surface during the rolling process.

In the PAV processes, CT30, which exhibits high volatile loss in the extended TFOT and CTO tests, shows low aging indices at all three process temperatures. The high pressure and relatively lower temperature limit the volatile loss. However, the asphalts (MA) with low volatile loss did show lower aging index than those (AM) with relatively higher volatile loss in the processes of PAV.

Table 5-7 shows the results of ANOVA and Duncan's tests on the logarithm of aging index at 60 °C. All three factors considered in the statistical model exhibited significant effects on the logarithm of aging index at 60 °C. A high R-Square of 0.9887 means that these three factors explain the variations very well. The interaction of asphalt and aging method is seen to have a significant effect on the aging index at 60 °C. This means that different aging methods are very likely to produce different aging severity on different asphalts. As an example, in the ranking of severity by the California Tilt Oven process for 168 hours, CT30 is the most severely aged asphalt as indicated by having the

Table 5-7 Results of ANOVA and Duncan's Multiple Range Test on the Logarithm of Aging Index at 60 °C in the Comparison of Different Aging Methods on Asphalt Cements

Dependent Variable: the Logarithm of Aging Index at 60 °C

Source	DF	Sum of Squares	Mean Squares	F Value	Pr > F
Model	84	26.29646585	0.31305316	88.86	0.0001
Error	85	0.29943865	0.00352281		
Corrected Total	169	26.59590449			

R-Square	C.V.	Root MSE	Overall Mean
0.988741	7.237151	0.059353	0.82011890

Source	DF	Anova SS	Mean Square	F Value	Pr > F
τ (asphalt)	4	0.43625002	0.10906251	30.96	0.0001
β (method)	16	25.03869809	1.56491863	444.22	0.0001
τβ(interaction)	64	0.82151773	0.01283621	3.64	0.0001

Duncan Grouping at fixed β:

β = TL		MA20	MA30	AM20	AM30	CT30
	Group	A	A	A	A	A
β = TS		MA30	MA20	CT30	AM20	AM30
	Group	A	A	A	A	A
β = TH		MA30	MA20	CT30	AM20	AM30
	Group	A	A	A	B	B
β = TLM		MA20	MA30	CT30	AM20	AM30
	Group	A	A	A	A	A
β = TSM		MA20	MA30	CT30	AM20	AM30
	Group	A	A	A	A	A
β = THM		MA20	MA30	CT30	AM20	AM30
	Group	A	A	B	C	C
β = TF10		MA30	MA20	CT30	AM30	AM20
	Group	A	A	A	A	A
β = TF15		MA20	MA30	CT30	AM20	AM30
	Group	A	A, B	A, B	B	C

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

Table 5-7 Continued

β = UV7	CT30	MA20	AM30	MA30	AM20
Group	A	A, B	B	B	B
β = UV14	AM30	CT30	MA30	MA20	AM20
Group	A	A, B	B	B	C
β = UV28	CT30	AM30	MA20	MA30	AM20
Group	A	A, B	A, B	A, B	B
β = C24	AM30	CT30	AM20	MA30	MA20
Group	A	A	A	A	A
β = C72	MA30	AM30	CT30	MA20	AM20
Group	A	A, B	A, B	A, B	B
β = C168	MA30	AM30	MA20	CT30	AM20
Group	A	B	B	B	B
β = P90	CT30	MA20	MA30	AM20	AM30
Group	A	A	A	A	A
β = P100	CT30	MA20	MA30	AM30	AM20
Group	A	B	B	B, C	C
β = P110	CT30	MA30	MA20	AM20	AM30
Group	A	A	A	B	B

Duncan Grouping at fixed τ:

τ = CT30	TL	TS	TLM	UV7	UV28	C24	UV14
Group	A	B	B	C	C, D	C, D	C, D
	TSM	TF10	TH	P100	P90	TF15	C72
Group	C, D	D, E	D, E	E	E	F	G
	P110	THM	C168				
Group	G	H	I				

τ = AM30	TL	TS	TLM	UV14	C24	UV28	UV7
Group	A	B	B	C	C, D	C, D	C, D
	TF10	TH	TSM	P90	P100	C72	TF15
Group	C, D	D	D	E	E	F	F
	C168	P110	THM				
Group	G	G	G				

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

Table 5-7 Continued

τ = AM20	TL	TS	TLM	C24	TH	TSM	UV28
Group	A	B	B	C	C	C	C
	UV7	TF10	UV14	P90	TF15	P100	C72
Group	C, D	C, D	D, E	E	F	G	H
	P110	THM	C168				
Group	I	I	I				
τ = MA30	TL	TS	TLM	TH	TSM	TF10	UV28
Group	A	B	B	C	C, D	C, D	C, D
	C24	UV14	UV7	P90	TF15	P100	C72
Group	C, D	D	D	E	E	E	F
	THM	P110	C168				
Group	F, G	G	H				
τ = MA20	TL	TLM	TS	TH	TSM	UV7	UV28
Group	A	B	B	C	C	C	C
	TF10	C24	UV14	P90	TF15	P100	THM
Group	C	C	C	D	D	D	E
	C72	P110	C168				
Group	E, F	F	G				

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

highest aging index at 60 °C as shown in Table 5-6. However in the method of PAV, it is the least severely aged asphalt no matter what process temperature is used.

The Duncan's test on the effect of asphalt (τ) at a fixed aging method (β) and that of aging method (β) at a fixed asphalt (τ) are shown in Table 5-7. The MA asphalts, which show low volatile loss during the TFOT processes, exhibit lower aging index in the process of TFOT and PAV, particularly at higher process temperature. This trend is also observed in the TFOT process using 25 g sample or longer exposure periods (15 hours). The effect of refinery source is significant when a higher process temperature is used in the TFOT and PAV. On the other hand, both UV chamber and California Tilt Oven are unable to differentiate the effect of refinery source.

5.3.5 Constant Stress Viscosity

Table A-4 and Table A-5 list the results of Schweyer Rheometer tests at 25 and 5 °C respectively. These data were used to calculate the corresponding aging indices, which are listed in Table 5-8 and Table 5-9 and plotted in Figure 5-5 and Figure 5-6. The highest aging index based on viscosity at 25 °C was found to be about 50, and that based on viscosity at 5 °C was 45, both resulting from the CTO process for 168 hours. This covers approximately the same range of values as the aging indices based on viscosity at 60 °C.

The results of ANOVA and Duncan's tests on the logarithm of aging indices at 25 and 5 °C are shown in Table 5-10 and Table 5-11, respectively. The R-Squares for these two parameters are 0.8948 and 0.8245, which are much lower than that for the aging index at 60 °C. It is caused by the insensitivity of the viscosity measurements at lower

Table 5-8 Aging Index at 25 °C of Residues of the Five Asphalts aged by the 17 Aging Processes

Laboratory Aging Process	Aging Index at 25 °C				
	CT30	AM30	AM20	MA30	MA20
TL	1.17	1.75	1.20	1.16	1.01
TS	2.08	2.25	1.47	1.73	1.70
TH	4.99	5.62	2.97	2.79	2.48
TLM	1.88	2.92	1.62	1.97	1.95
TSM	5.25	5.02	2.54	3.58	3.22
THM	16.37	12.17	7.67	7.86	7.64
TF10	4.94	4.95	3.23	2.79	2.60
TF15	6.81	7.48	4.34	3.79	3.58
UV7	3.48	4.05	4.34	3.72	3.49
UV14	8.12	4.12	3.57	4.37	4.03
UV28	5.49	3.64	4.10	5.24	3.18
C24	4.49	4.12	2.87	4.14	4.04
C72	14.99	11.23	10.79	9.84	10.24
C168	49.73	39.66	28.75	16.66	29.69
P90	7.03	8.46	5.56	5.08	5.05
P100	6.72	9.00	7.83	7.86	6.61
P110	21.13	24.28	16.74	10.86	11.69

Note:

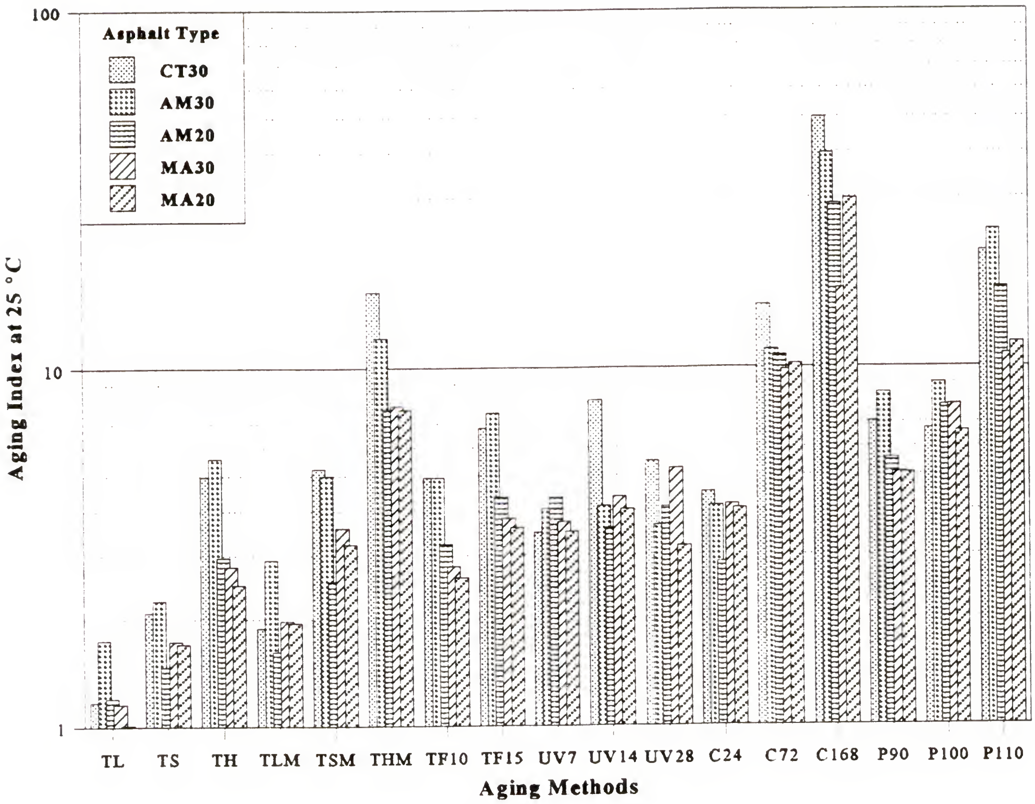
See Table 3-1 and Table 3-2 for the meaning of codes.

Table 5-9 Aging Index at 5 °C of Residues of the Five Asphalts aged by the 17 Aging Processes

Laboratory Aging Process	Aging Index at 5 °C				
	CT30	AM30	AM20	MA30	MA20
TL	1.36	1.06	1.10	1.36	1.66
TS	2.20	1.72	1.55	1.46	2.22
TH	4.98	3.41	2.85	3.30	4.03
TLM	2.10	1.85	1.54	2.24	1.97
TSM	4.67	4.14	2.80	3.90	6.49
THM	10.92	7.61	7.31	7.94	7.99
TF10	4.55	2.41	2.65	3.43	3.01
TF15	6.63	2.66	3.41	4.54	4.25
UV7	4.57	3.17	3.24	4.93	4.38
UV14	3.81	3.25	2.75	6.55	3.95
UV28	4.08	3.36	2.47	3.78	4.66
C24	5.39	4.44	3.02	5.08	4.56
C72	19.97	9.45	8.84	12.98	8.34
C168	35.46	32.60	45.73	17.37	35.90
P90	10.73	9.95	5.65	5.47	3.35
P100	10.97	7.66	7.67	10.97	5.42
P110	21.15	30.57	17.52	11.64	9.30

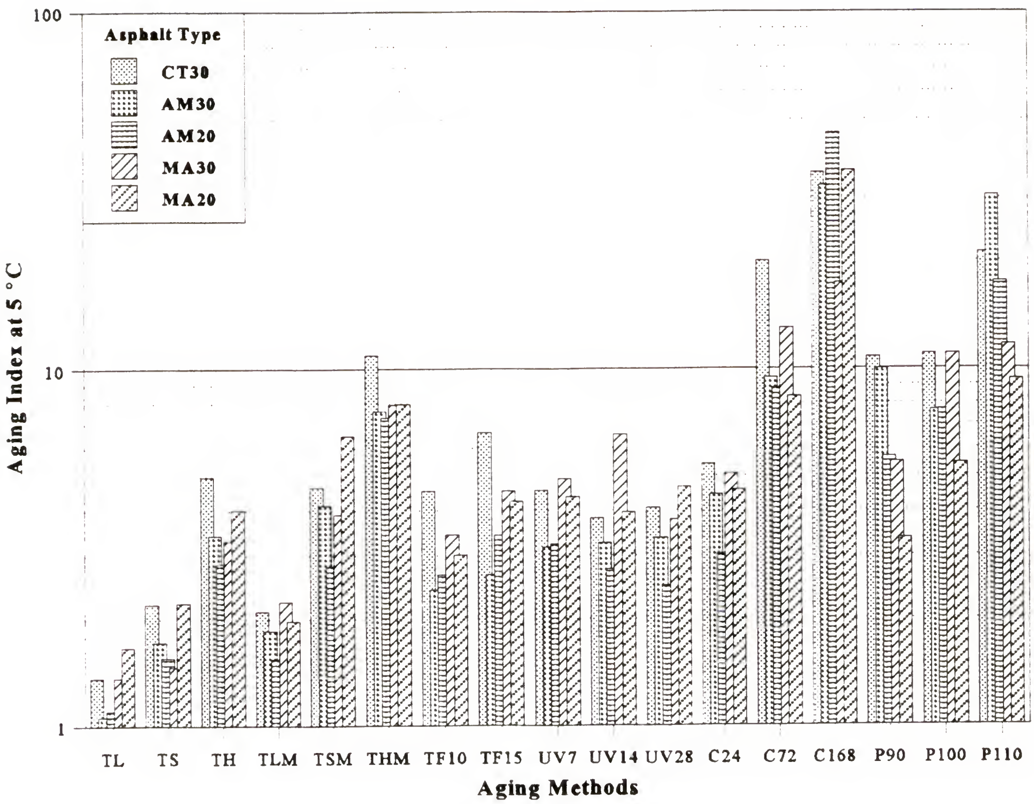
Note:

See Table 3-1 and Table 3-2 for the meaning of codes.



Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Figure 5-5 Aging Index at 25 °C of the Residues of the Five Asphalts Aged by the 17 Aging Methods



Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Figure 5-6 Aging Index at 5 °C of the Residues of the Five Asphalts Aged by the 17 Aging Methods

Table 5-10 Results of ANOVA and Duncan's Multiple Range Test on the Logarithm of Aging Index at 25 °C in the Comparison of Different Aging Methods on Asphalt Cements

Dependent Variable: Carbonyl Ratio Index

Source	DF	Sum of Squares	Mean Squares	F Value	Pr > F
Model	84	21.03962102	0.25047168	8.60	0.0001
Error	85	2.47451959	0.02911200		
Corrected Total	169	23.51414061			

R-Square	C.V.	Root MSE	Overall Mean
0.894765	24.56302	0.170622	0.69463110

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Asphalt (τ)	4	0.89623226	0.22405806	7.70	0.0001
Method (β)	16	19.24866855	1.20304178	41.32	0.0001
Interaction ($\tau\beta$)	64	0.89472021	0.01398000	0.48	0.9988

Duncan Grouping	Mean	N	Asphalt
A	0.8086	34	AM30
A			
A	0.7513	34	CT30
B	0.6519	34	AM20
B			
B	0.6399	34	MA30
B			
B	0.6215	34	MA20

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

Table 5-10 Continued

Duncan Grouping		Mean	N	Method
	A	1.4920	10	C168
	B	1.1907	10	P110
	B			
C	B	1.0585	10	C72
C				
C	D	0.9969	10	THM
	D			
E	D	0.8655	10	P100
E				
E	F	0.7714	10	P90
	F			
G	F	0.6830	10	TF15
G	F			
G	F	0.6479	10	UV28
G				
G		0.5960	10	C24
G				
G		0.5888	10	UV14
G				
G		0.5809	10	TSM
G				
G		0.5659	10	UV7
G				
G		0.5588	10	TH
G				
G		0.5401	10	TF10
	H	0.3086	10	TLM
	H			
	H	0.2659	10	TS
	I	0.0977	10	TL

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

Table 5-11 Results of ANOVA and Duncan's Multiple Range Test on the Logarithm of Aging Index at 5 °C in the Comparison of Different Aging Methods on Asphalt Cements

Dependent Variable: Carbonyl Ratio Index

Source	DF	Sum of Squares	Mean Squares	F Value	Pr > F
Model	84	21.71677778	0.25853307	4.75	0.0001
Error	85	4.62243893	0.05438163		
Corrected Total	169	26.33921671			

R-Square	C.V.	Root MSE	Overall Mean
0.824504	33.18095	0.233199	0.70280902

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Asphalt (τ)	4	0.44995923	0.11248981	2.07	0.0920
Method (β)	16	19.54055203	1.22128450	22.46	0.0001
Interaction ($\tau\beta$)	64	1.72626652	0.02697291	0.50	0.9981

Duncan Grouping		Mean	N	Asphalt
	A	0.8034	34	CT30
	A			
B	A	0.6979	34	MA30
B				
B		0.6760	34	AM30
B				
B		0.6701	34	MA20
B				
B		0.6667	34	AM20

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

Table 5-11 Continued

Duncan Grouping		Mean	N	Method
	A	1.503	10	C168
	B	1.229	10	P110
	B			
C	B	1.064	10	C72
C				
C	D	0.933	10	THM
C	D			
C	D	0.917	10	P100
	D			
E	D	0.809	10	P90
E				
E	F	0.657	10	C24
E	F			
E	F	0.633	10	TSM
E	F			
E	F	0.625	10	TF15
E	F			
E	F	0.608	10	UV28
E	F			
E	F	0.607	10	UV7
E	F			
E	F	0.603	10	UV14
E	F			
E	F	0.572	10	TH
	F			
	F	0.511	10	TF10
	G	0.299	10	TLM
	G			
	G	0.252	10	TS
	G			
	G	0.125	10	TL

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.

temperatures. Thus the interaction effect is not significant based on these two parameters. The Duncan's groupings on different aging methods, based on the aging index at 25 and 5 °C, are in a general agreement with that grouped by the aging index at 60 °C.

The major concern on age hardening study is on the low temperature property. The constant-stress viscosity at 5 °C of the different aged asphalts were plotted in Figure 5-7. An empirical viscosity limit of 2×10^{10} poises in avoiding thermal cracking problem are used in this study. As shown in Figure 5-7, six residues exhibit a viscosity value exceeding this limit. They are:

(1) CT30 after the California Tilt Oven for 168 hours.

(2) AM20 after the California Tilt Oven for 168 hours.

(3) AM30 after the California Tilt Oven for 168 hours.

(4) AM30 after standard TFOT and the Pressure Aging Vessel at 110 °C.

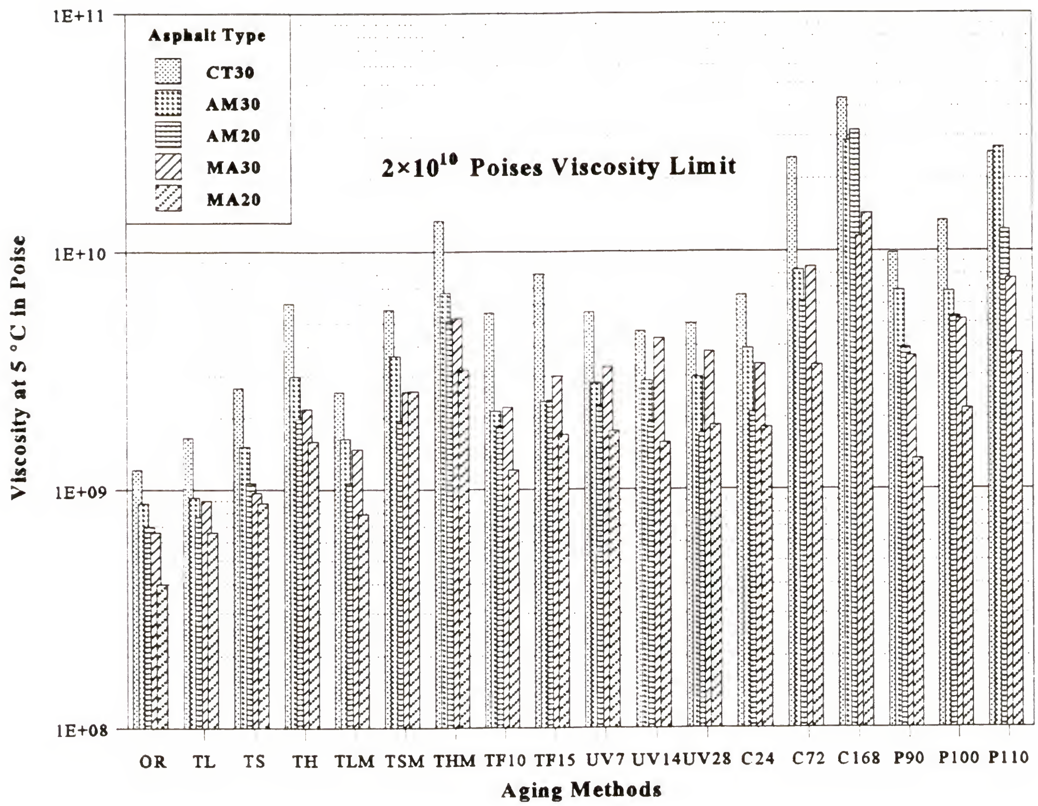
(5) CT30 after standard TFOT and the Pressure Aging Vessel at 110 °C.

(6) CT30 after the California Tilt Oven for 72 hours.

5.3.6 Temperature Susceptibility

Two conventional temperature susceptibility, $PVN'_{(25\text{-}60)}$ and *VTS (60-5)* were evaluated in this study. The absolute viscosity at 60 °C and the constant stress viscosity at 5 °C were used to calculate *VTS (60-5)* according to Equation 5. The penetration at 25 °C and absolute viscosity at 60 °C were used to calculate $PVN'_{(25\text{-}60)}$ according to Equation 7.

Table 5-12 and Table 5-13 list these two parameters of the five asphalts and their residues aged by the 17 aging methods. All the 17 aging methods have the same effect of



Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Figure 5-7 Constant Stress (1MPa) Viscosity at 5 °C of the Residues of the Five Asphalts Aged by the 17 Aging Methods

Table 5-12 Temperature Susceptibility Parameter, $PVN'_{(25-60)}$, of the Five Asphalts and their Residues Aged by the 17 Aging Methods

Laboratory Aging Process	*PVN' (25-60)*				
	CT30	AM30	AM20	MA30	MA20
Original	-0.57	-0.40	-0.50	-0.52	-0.52
TL	-0.41	-0.32	-0.43	-0.38	-0.43
TS	-0.38	-0.15	-0.27	-0.32	-0.40
TH	-0.18	0.34	0.08	-0.08	-0.10
TLM	-0.08	0.20	0.14	-0.01	-0.09
TSM	0.27	1.02	0.52	0.36	0.13
THM	-0.32	-0.03	-0.23	-0.29	-0.46
TF10	-0.29	0.26	0.09	-0.13	-0.22
TF15	0.74	1.44	1.04	0.63	0.52
UV7	-0.23	0.11	0.07	0.04	-0.11
UV14	-0.06	-0.11	0.19	-0.04	-0.08
UV28	-0.22	0.04	-0.01	-0.04	-0.14
C24	-0.11	0.03	0.03	0.03	-0.05
C72	0.43	0.61	0.62	0.51	0.53
C168	0.83	1.08	1.02	0.83	0.95
P90	-0.05	0.40	0.23	0.17	0.06
P100	-0.12	0.50	0.47	0.27	0.13
P110	0.54	1.18	1.12	0.66	0.53

Note:

$PVN'_{(25-60)}$ is calculated according to Equation 7 in Chapter 3.
See Table 3-1 and Table 3-2 for the meaning of codes.

Table 5-13 Temperature Susceptibility Parameter, *VTS (60-5)*, of the Five Asphalts and their Residues Aged by the 17 Aging Methods

Laboratory Aging Process	*VTS (60-5)*				
	CT30	AM30	AM20	MA30	MA20
Original	3.92	3.81	3.91	3.76	3.79
TL	3.80	3.62	3.74	3.66	3.75
TS	3.77	3.57	3.64	3.56	3.62
TH	3.62	3.38	3.46	3.47	3.52
TLM	3.61	3.35	3.38	3.40	3.39
TSM	3.46	2.90	3.21	3.24	3.29
THM	3.75	3.56	3.63	3.59	3.61
TF10	3.66	3.41	3.45	3.45	3.59
TF15	3.15	2.79	2.89	3.07	3.17
UV7	3.73	3.42	3.44	3.40	3.49
UV14	3.62	3.53	3.31	3.49	3.40
UV28	3.68	3.46	3.41	3.49	3.48
C24	3.68	3.55	3.49	3.45	3.44
C72	3.43	3.22	3.18	3.25	3.10
C168	3.19	3.16	3.20	3.08	3.07
P90	3.63	3.44	3.44	3.33	3.24
P100	3.60	3.33	3.39	3.30	3.30
P110	3.45	3.30	3.24	3.15	3.10

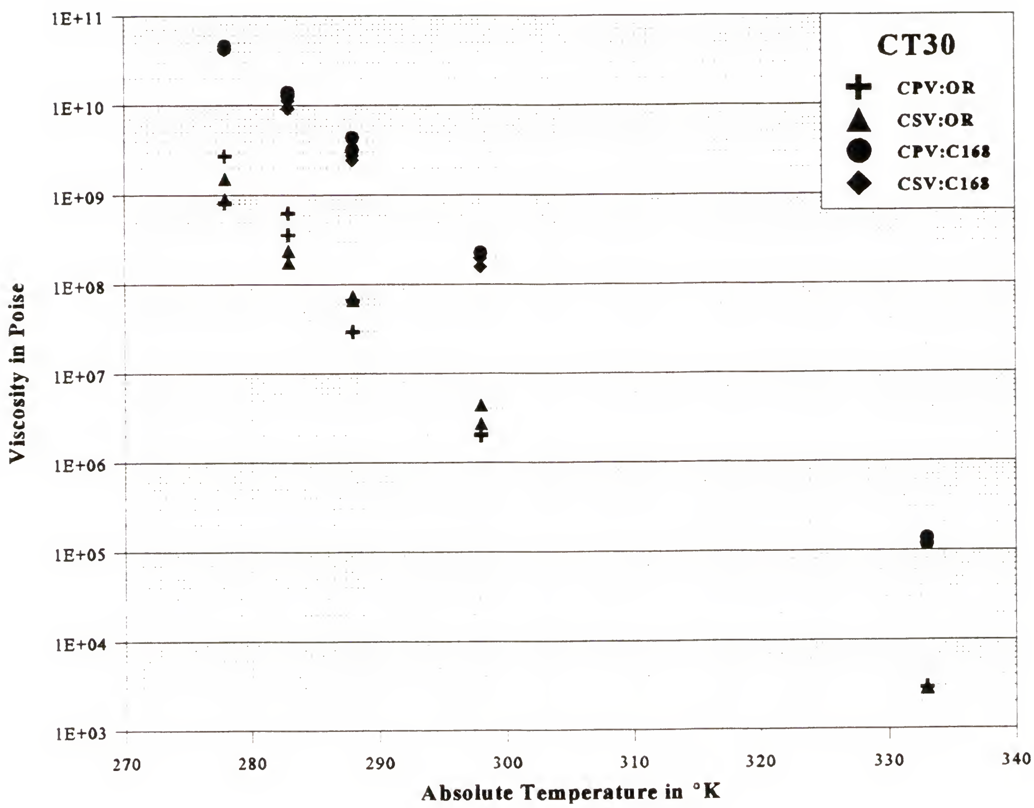
Note:

VTS (60-5) is calculated according to Equation 5 in Chapter 3.
See Table 3-1 and Table 3-2 for the meaning of codes.

increasing $PVN'_{(25\text{-}60)}$ and decreasing $VTS\ (60\text{-}5)$. This implies that the temperature susceptibility of an asphalt reduces with age hardening. The higher the degree of aging, the lower the temperature susceptibility would become. As can be seen in Table 5-12 and Table 5-13, CT30 is the most temperature susceptible asphalt among the five asphalts used in this study, before or after any of the 17 aging processes.

To investigate the parallel shift pattern in the log-log plot of viscosity versus temperature, the Schweyer Rheometer tests were performed (with two replicates) at two additional temperatures, namely 15 and 10 °C, on the five asphalts and their residues aged by the California Tilt Oven for 168 hours. Figure 5-8 through 5-12 show the plots of viscosity versus absolute temperature for the five asphalts used in this study. It is assumed that asphalts have Newtonian flow behavior at 60 °C and the constant power viscosity (CPV) or constant stress viscosity (CSV) at 60 °C is equal to the absolute viscosity. The linear scale is used for the temperature to make the figures more readable. With some variation, the parallel shift pattern are generally observed for all five asphalts as shown in Figure 5-8 through Figure 5-12.

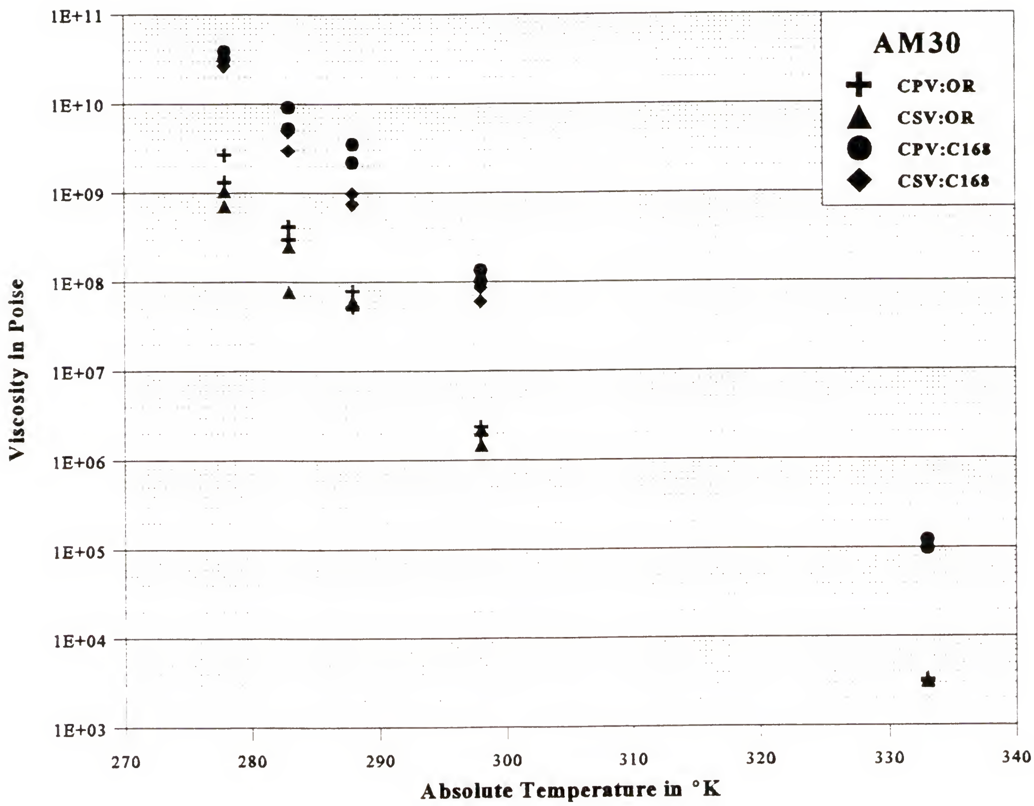
Linear regression analyses were performed to estimate the viscosity-temperature relationship for the different asphalts before and after CTO aging for 168 hours, which is the most severe aging method used in this study. The purpose of these analyses is to determine how these relationships may change with aging. The summary of the results of the regression analyses are shown in Table 5-14. The slope (β_1 in Equation 8) of the regression line represents the temperature susceptibility of asphalt. The following conclusion were drawn from these analyses:



Note:

CPV- Constant Power Viscosity.
CSV- Constant Stress (1MPa) Viscosity.
OR- Original.
C168- California Tilt Oven process for 168 hours.

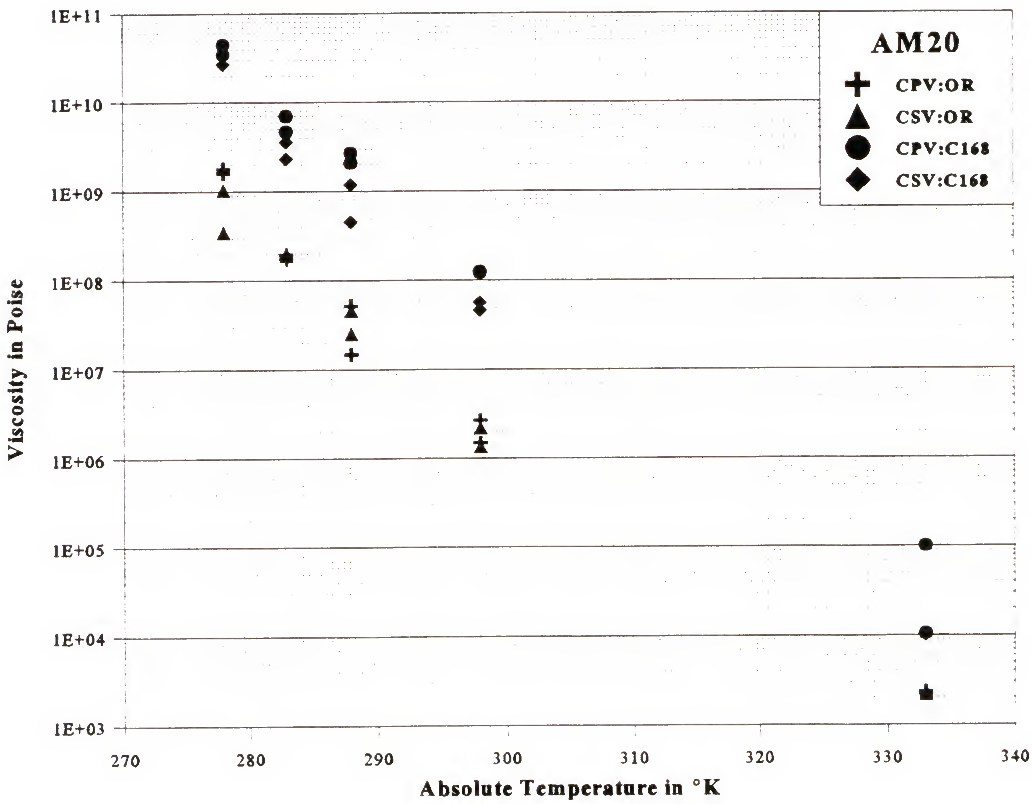
Figure 5-8 Viscosity versus Absolute Temperature for CT30 Asphalt



Note:

CPV- Constant Power Viscosity.
CSV- Constant Stress (1MPa) Viscosity.
OR- Original.
C168-California Tilt Oven process for 168 hours.

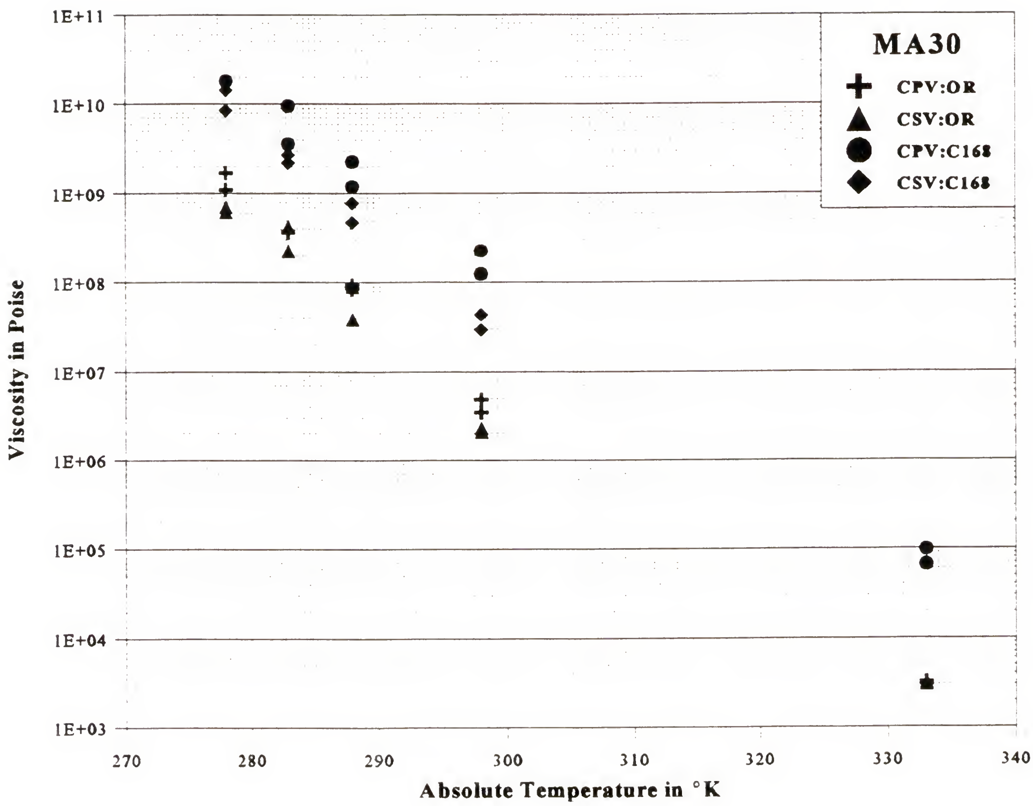
Figure 5-9 Viscosity versus Absolute Temperature for AM30 Asphalt



Note:

CPV- Constant Power Viscosity.
CSV- Constant Stress (1MPa) Viscosity.
OR- Original.
C168- California Tilt Oven process for 168 hours.

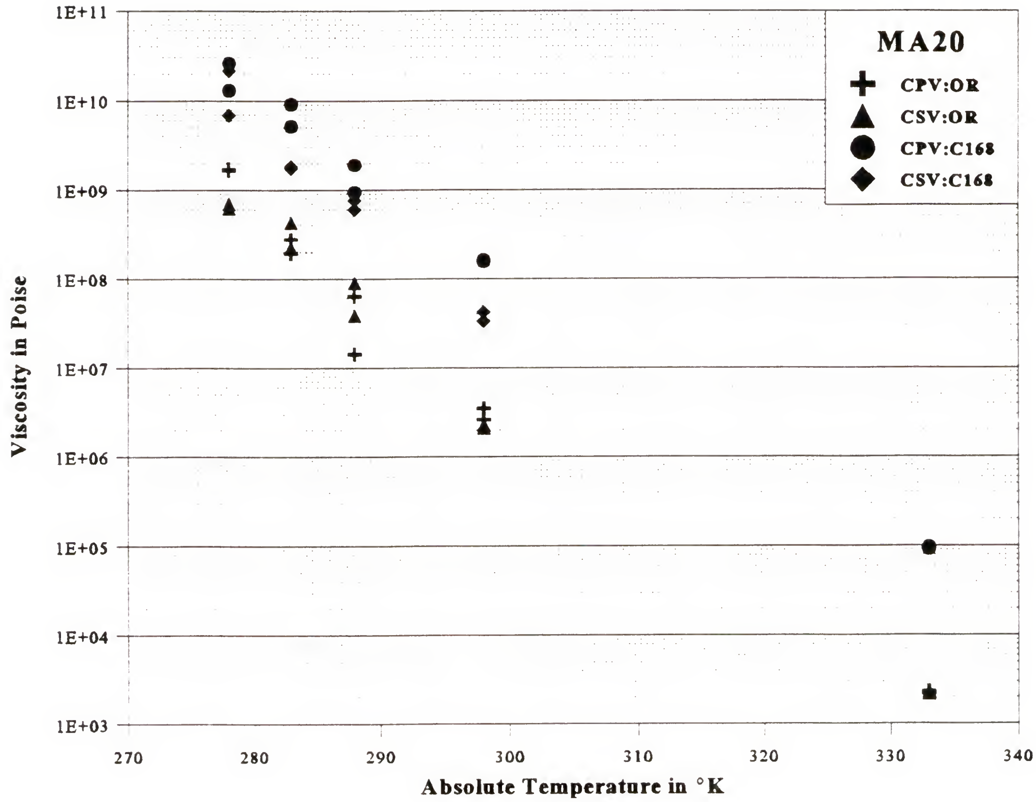
Figure 5-10 Viscosity versus Absolute Temperature for AM20 Asphalt



Note:

CPV- Constant Power Viscosity.
CSV- Constant Stress (1MPa) Viscosity.
OR- Original.
C168- California Tilt Oven process for 168 hours.

Figure 5-11 Viscosity versus Absolute Temperature for MA30 Asphalt



Note:

CPV- Constant Power Viscosity.
CSV- Constant Stress (1MPa) Viscosity.
OR- Original.
C168- California Tilt Oven process for 168 hours.

Figure 5-12 Viscosity versus Absolute Temperature for MA20 Asphalt

Table 5-14 Results of Linear Regression Analysis Results on the Viscosity-Temperature Relationships of the Five Asphalts before and after CTO aging for 168 hours

Regression Equation: (Equation 8 in Chapter 2)

$$log(\eta_{100}) = \beta_0 - \beta_1 \, log(T)$$

Constant Power Viscosity

Asphalt		CT30	AM30	AM20	MA30	MA20
Original Asphalt	β_0	185.703	185.617	183.755	184.074	188.318
	β_1	72.722	72.672	71.988	72.023	73.770
	Std*	4.129	3.606	3.948	1.846	2.610
	R^2	0.9749	0.9807	0.9765	0.9948	0.9901
C168 Aged Residue	β_0	183.536	179.815	180.062	176.400	174.551
	β_1	71.031	69.716	69.825	68.380	67.629
	Std*	0.972	2.023	1.913	1.692	1.625
	R^2	0.9985	0.9933	0.9940	0.9951	0.9954

Constant-Stress Viscosity

Asphalt		CT30	AM30	AM20	MA30	MA20
Original Asphalt	β_0	180.566	174.985	177.277	177.207	172.201
	β_1	70.644	68.437	69.397	69.310	67.386
	Std*	1.980	3.193	2.851	2.890	2.615
	R^2	0.9938	0.9829	0.9867	0.9863	0.9881
C168 Aged Residue	β_0	180.635	171.935	171.969	166.684	163.773
	β_1	70.011	66.614	66.653	64.584	63.403
	Std*	1.290	2.833	3.726	2.660	2.959
	R^2	0.9973	0.9857	0.9756	0.9866	0.9829

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.

* : Standard error of β_1 with a degree of freedom of 8.

(1) Good linear relationships (R-Square > 0.97) were found between the logarithm of viscosity (both constant-power and constant-stress) and the logarithm of absolute temperature in °K.

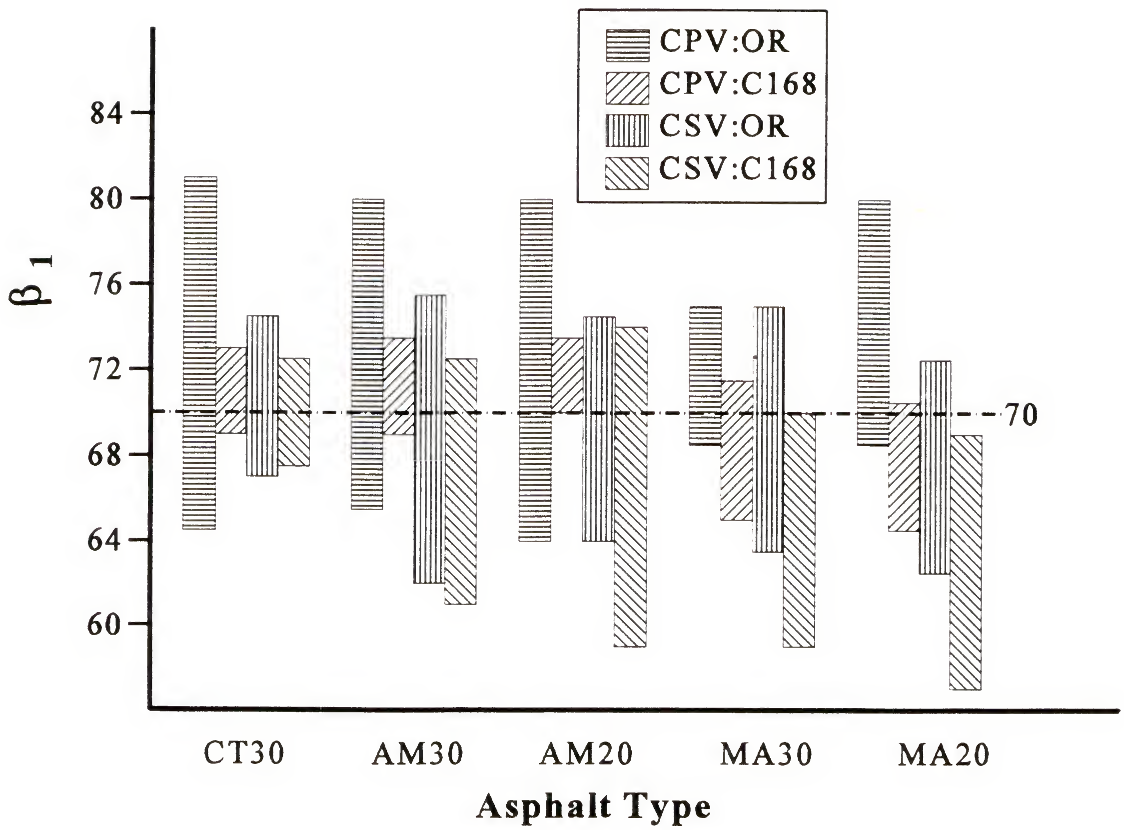
(2) The five asphalts used in this study have similar temperature susceptibilities, which could be represented by a β_1 value of 70 as shown in Figure 5-13.

(3) The temperature susceptibility (in the range of 5 to 60 °C) of the aged residues after the CTO process for 168 hours decreases slightly, and the reduction is statistically insignificant at $\alpha = 0.05$.

It is to be noted that the temperature range considered is extremely narrow in the logarithm scale and viscosity measurements at low temperatures have a high variation. A higher variation is therefore occurring for both β_0 and β_1, although a high R-Square is obtained in the regression analysis. Furthermore, asphalt behave as a non-Newtonian flow at low temperatures, that is, the viscosity is also a function of shear rate. Different shear rates are used in the penetration, absolute viscosity, and Schweyer rheometer tests. Therefore the temperature susceptibility is difficult to be clearly defined.

5.4 Comparison of Evaluation Parameters

The aging effects of different aging methods have been evaluated by different parameters used in this study. Although the relative aging severity rankings among the 17 aging methods are in a general agreement on the basis of the percent penetration retained, aging indices at different temperatures, and carbonyl ratio index, there are some discrepancies. The high temperature TFOT on 25 g samples produces similar aging severity as the PAV process at 110 °C in terms of aging index at 60 °C. In terms of



Note:

See Table 3-1 and Figure 5-11 for the meaning of codes.

Figure 5-13 The 95% Confidence Intervals of β_1 Values in the Regression Analysis of Viscosity-Temperature Relationship

carbonyl ratio index, the PAV process at 110 °C produces higher oxidation than the high-temperature TFOT 0n 25 g samples.

As far as aging severity of asphalts is concerned, a better evaluation parameter should be able to differentiate different degrees of age hardening. Since the same statistical model was used for different evaluation parameters, the coefficient of variation (C.V.) in the ANOVA tables can be used to compare the ability of the parameter for differentiating the aging severity. The coefficient of variation of viscosity measurements increases with the reduction of testing temperature as shown in Table 5-15. The variations of the model are generally well explained by these five parameters with R-Square values over 0.8. The logarithm of aging index at 60 °C is found to be the most sensitive parameter in detecting differences in aging severity.

Higher weight loss of the aged asphalt was measured after the processes of TFOT at high temperature and higher weight gain was measured after the process of PAV at higher temperature. Some asphalts showed a small amount of weight gain in the process of CTO and the others showed weight loss. The possible dehydrogenation at high temperature are not detectable by the evaluation parameters used in this study.

5.5 Advantages and Disadvantages of Different Aging Processes

Based on the results of this study, the advantages and disadvantages of different aging processes can be summarized in Table 5-16. The advantages of the extended TFOT include the conveniences of using the standard equipment and hardening asphalts to a higher degree within a short time (five hours). In terms of the aging index at 60 °C, an average value of 25 , which is similar to that of PAV at 110 °C, can be obtained by using

Table 5-15 Comparison of the Coefficient of Variation of the Different Parameters as Determined form the Analysis of Variance

Evaluation Parameters	Coeficient of Variation (%)
Percent Penetration Retained	9.009738
Carbonyl Ratio Index	11.91475
log (Aging Index at 60 °C)	7.237151
log (Aging Index at 25 °C)	24.56302
log (Aging Index at 5 °C)	33.18095

Note:

Model $Y_{ijk} = \mu + \tau_i + \beta_j + \tau\beta_{ij} + \epsilon_{ijk}$ (Equation 12 on page 78)
$i = 1$ to 5, $j = 1$ to 17, degree of freedom of error = 85.

Table 5-16 Summary of Comparison of Different Aging Methods Investigated in this Study

Comparison of Different Aging Methods				
Item	**Extended TFOT**	**UV Chamber**	**California Tilt Oven**	**Pressure Aging Vessel**
Precondition	No	TFOT	No	TFOT*
Sample size per batch	50 or 25 g pans, up to 5 pans	25 g pans, up to 40 pans	35 g bottles, up to 8 bottles	50 g pans. up to 10 pans
Testing temperature in ° C	140, 163, and 185	60	111	90, 100. and 110
Processing Time	5, 10, 15 hours	7, 14, 28 days	24, 72, 168 hours	20 hours
Approximate aging index at 60 °C	25 for 5 hours at 185 °C	5	4.5, 16, 38 for 24, 72, 168 hours	7.5, 9.5, 25 for 90, 100, 110 °C
Advantages	Standard equipment, short processing time, severe aging.	Low temperature aging, effect of light.	Standard equipment, relatively lower temperature.	Limiting volatile loss, high degree aging at short time, large quantity of samples.
Disadvantages	High volatile loss, formation of skin.	UV affect only the top surface, long processing time.	Severity related to initial viscosity, long processing time.	New equipment, require great care in operation.

Note:

*: TFOT was used as precondition of the PAV Process in this study. RTFOT was suggested by SHRP.

the 25-g TFOT at 185 °C. The disadvantages are the high volatile loss and the formation of skin on the sample.

The advantages of using UV Chamber are the low process temperature and the consideration of the effects of UV light. The disadvantage are the long processing time and the fact that light affects only the top surface of the sample. A large exposure surface with thinner asphalt film should be used to obtain a more severe aging. If a thin film is used, the collection of the aged residue for the binder tests could be a problem.

The advantages of the California Tilt Oven are the conveniences of using the standard equipment and aging at a relatively lower temperature. It was found to be the most severe aging method in this study. The disadvantages are the fact that the aging severity is related to initial viscosity of the sample, and the relatively long processing time.

The advantages of the Pressure Aging Vessel are high degree of aging at short time, producing large quantity of aged samples, and the fact that it limits the volatile loss. The disadvantages are the reluctance of accepting a new set of equipment and its great care in operation, and the possibility that the aging effect is not severe enough for some hot environment.

5.6 Summary of Findings

Four laboratory accelerated aging procedures, which were promising in the simulation of long-term aging of asphalts, were investigated on the conventional asphalts commonly used in Florida. Different parameters obtained from the binder tests were used to evaluate the aging severity of asphalts after different aging processes. The following conclusions were derived from these research efforts:

(1) Different asphalts could age differently in different aging processes. The ranking of aging severity on different asphalts could be different by using different evaluation parameters.

(2) Asphalts generally exhibit higher weight loss at high temperature TFOT and higher weight gain at high temperature PAV. The volatile loss does not seem to dominate the age hardening of asphalts in the process of TFOT at higher temperature.

(3) Due to the insensitivity of consistency measurements at lower temperature, the most sensitive parameter for characterizing the aging severity of asphalt binders was found to be the aging index at 60 °C, which is the ratio of absolute viscosities at 60 °C.

(4) The conventional temperature susceptibility parameters, *PVN'* and *VTS*, were found to change after age hardening. Asphalts become less temperature susceptible after aging according to these two parameters.

(5) The β_1 value, which is the slope of the regression line in the log-log plot of viscosity versus absolute temperature, was essentially the same before and after aging.

(6) The asphalt residues after aging in the CTO, PAV, and high temperature TFOT all have high carbonyl ratio indices. Though no particular aging pattern was found in the process of high temperature TFOT, the formation of skin and its subsequent retarding of further aging could be the major drawback of this process.

(7) There was no significant additional hardening of the asphalt residues from 7 days to 28 days exposure in the UV Chamber. Only the surface of the asphalt samples was aged by the UV light in the UV Chamber.

(8) The California Tilt Oven was found to be the most severe aging method in this study. However, low-viscosity asphalts were found to age more in the CTO process due to a larger contact surface caused by higher mobility in the rolling process.

(9) The advantages of the Pressure Aging Vessel are high degree of aging at short time, producing large quantity of aged samples, and the fact that it limits the volatile loss. The disadvantages are the reluctance of accepting a new set of equipment and its great care in operation, and the possibility that the aging effect is not severe enough for some hot environment.

CHAPTER 6
AGING CHARACTERISTICS OF MODIFIED BINDERS

6.1 Introduction

A testing program was performed to investigate the effects of different modifiers on the aging characteristics of the asphalt binders. The major possible benefits of modified asphalts to be investigated in this study are on the reduction of aging potential and the lower viscosity value at low temperatures due to the reduction of temperature susceptibility. Two kinds of aging processes, CTO and PAV, were selected to harden the modified binders, and the binder tests as used in Chapter 5 were performed on both the unaged binders and their aged residues. Due to the fact that different asphalts produce different aging severity in different aging processes, the CTO data and the PAV data were analyzed separately. The Brookfield rheometer was evaluated for its possibility of replacing the capillary tube viscometer. To investigate the possible difference between a TFOT and a RTFOT treatment of the asphalt samples in the PAV process, a comparison of these two procedures was conducted.

6.2 Materials and Laboratory Procedures

Five modifiers, as listed earlier in Table 3-1, which include fine ground tire rubber (GTR), carbon black (CB), styrene ethylene butylene styrene (SEBS), ethylene vinyl acetate (EVA), and styrene butadiene rubber (SBR) were blended at adequate dosage

levels with an AC-30 to produce five blends of modified AC-30 asphalts. These modified binders were subjected to the California Tilt Oven and Pressure Aging Vessel aging processes, and their aged residues were tested for evaluating the effect of modifiers on the aging characteristics of the asphalt binders. Penetration, absolute viscosity, Schweyer rheometer test, and infrared spectral analysis were performed on both unaged binders and aged residues.

The optimum dosages of the different modifiers to be used were based on the findings from another research project at the University of Florida [65]. The SEBS and EVA modified binders were blended by the company which supplied the modifiers. The fine ground tire rubber, carbon black, and SBR modified binders were blended at the laboratory of University of Florida. No special problems were encountered in blending the fine ground tire rubber and the carbon black with AC-30 asphalt. When the SBR was added to the AC-30, the water in the SBR would cause an explosive vaporization. Thus, it was necssary to add the SBR very slowly to the asphalt during blending.

The homogeneity of most modified binders is generally achieved in the blending process. In the storage period, carbon black in the modified binder was found to accumulate at the bottom of container, and thus the modified asphalt needed to be thoroughly blended before use. In the process of California Tilt Oven and RTFOT, the carbon black deposit could not be completely poured out of the bottle and a lower carbon black content was expected in the CTO aged residue. In the process of TFOT+PAV, the aged residues were scraped out of the TFOT pans by using a hard cardboard. The

infrared spectral analysis is not applicable on the carbon black modified binders because of the occurrence of too many peaks in the spectrum.

The SEBS, EVA, and SBR modified binders tend to show some degree of inconsistency after several times of heating. The SBR modified binder exhibited a strong cohesion, and was difficult to be stirred and poured. A great care is therefore necessary for preparing these testing samples. The SBR modified binders exhibited a high degree of expansion while being forced to flow through the capillary tube in the Schweyer rheometer tests as shown in Figure 6-1 (A). Some of the residues of SEBS modified binders showed a similar behavior. The high compressibility of these asphalts makes the basic assumptions of the Schweyer rheometer test invalid. The rod-climbing effects, as shown in Figure 6-1 (B), were found in the Brookfield rotational viscosity test on the SBR modified binders and some EVA residues. The up-climbing of asphalt sample changes the shearing area of the spindle and make the calculation of viscosity incorrect. These samples were decided to be tested in the Brookfield rheometer at only one shear rate (1 sec^{-1}) and data were obtained at one minute, when a severe rod-climbing phenomena had not yet occurred.

Some modified binders such as SEBS modified binder have a original penetration of 24 and the minimum measured penetration of about 14 after the CTO process. This represents a penetration retained percentage of more than 50. Thus, most modified asphalts will have a higher percentage of penetration retained due to a lower initial penetration value. It is obvious that the penetration retained is not adequate to represent the aging severity of modified binders due to the insensitivity of consistency measurements at the low penetration (high viscosity) condition. Similar results were found on the low

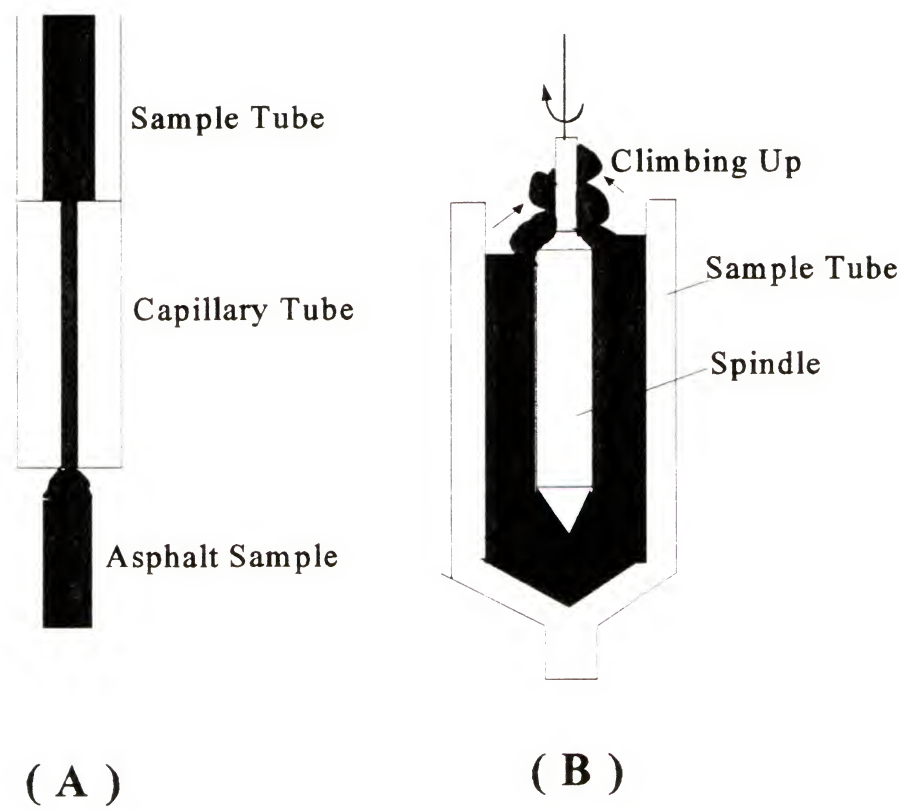


Figure 6-1 The Expansion of SBR Modified Binder in the Schweyer Rheometer Test (A) and the Rod-Climbing Phenomena in the Brookfield Rheometer Test (B)

temperature viscosities obtained from the Schweyer tests. The absolute viscosity at 60 °C is used as the major evaluation parameter for the study of aging severity.

All five modified binders could not completely spread out and cover the flask in the processes of California Tilt Oven. The flask-covering range depended on the viscosity of the asphalt binders at 111 °C. Most conventional asphalts (AC-30 and AC-20) could cover up to 2/3 of the flasks while modified binders could cover only from 1/2 to 1/4 of the bottles. The purpose of the 1 °C tilt of the oven did not seem to be necessary for the asphalt binders used in this study. The 1 °C tilting, however, was maintained for all CTO tests in this study.

Air bubbles were formed on the surface of most asphalt samples aged by the PAV processes. Asphalts aged at a higher process temperature generally displayed more bubbles than those aged at a lower process temperature. Some modified binders, such as those modified with SEBS, EVA, and SBR, exhibited a capacity of preventing the formation of air bubbles. An additional heating and stirring were applied to the aged samples to remove the air bubble in the preparation of the samples for the binder tests.

6.3 Test Results

Appendix B lists the test results of modified binders and their aged residues by CTOs and PAVs. The SBR modified binder was not included in the binders aged by the processes of CTO. The summary of results of tests on modified asphalts which were aged by the CTO and PAV processes, are listed in Table 6-1 and Table 6-2, respectively. These two aging processes were performed at similar temperatures. CTO process provides

Table 6-1 Summary of Results of Tests on the CTO Residues of Modified Asphalts

Process Time in Hour	Asphalt Type				
	CT30	GTR	CB	SEBS	EVA
Penetration at 25 °C in 1/100 cm					
0	56	46	48	24	40
24	30	28	27	21	22
72	19	19	18	16	17
168	14	17	14	14	11
Absolute Viscosity at 60 °C in poise					
0	2883	5922	4600	24944	4880
24	12194	23772	13512	58784	20757
72	47250	53950	36584	83776	92725
168	127756	122240	97678	145675	1909352
Constant Stress (1MPa) Viscosity at 25 °C in 10^6 poises					
0	3.58	1.84	2.39	22.15	6.38
24	16.10	28.45	17.65	44.70	10.15
72	53.80	38.65	45.10	84.10	24.15
168	178.00	92.35	89.55	154.00	70.50
Constant Stress (1MPa) Viscosity at 5 °C in 10^9 poises					
0	1.22	1.00	0.87	5.30	5.56
24	6.56	6.54	4.18	6.21	8.37
72	24.40	9.29	15.65	13.00	9.90
168	43.20	15.05	39.45	71.45	39.75
Carbonyl Ratio					
0	0.3083	0.3214	-	0.3044	0.3874
24	0.4350	0.4185	-	0.3015	0.4484
72	0.4805	0.5380	-	0.3877	0.5968
168	0.5662	0.5676	-	0.4427	0.7116

Note:

See Table 3-1 for the meaning of codes.

Table 6-2 Summary of Results of Tests on the PAV Residues of Modified Asphalts

Process Temperature in °C	Asphalt Type					
	CT30	GTR	CB	SEBS	EVA	SBR
Penetration at 25 °C in 1/100 cm						
Original	56	46	48	24	40	-
90	24	24	22	24	44	41
100	23	22	20	21	22	42
110	19	18	16	18	20	37
Absolute Viscosity at 60 °C in poise						
Original	2883	5922	4600	24944	4880	7404
90	18699	34476	27540	100950	38392	26411
100	18321	45204	40827	139257	58999	38861
110	53796	88388	87361	278470	195354	56813
Constant Stress (1MPa) Viscosity at 25 °C in 10^6 poises						
Original	3.58	3.52	2.39	22.15	6.38	1.02
90	21.20	35.05	30.70	115.00	23.00	2.56
100	25.90	40.15	49.60	160.00	19.80	6.32
110	71.30	77.80	84.55	198.00	72.40	10.60
Constant Stress (1MPa) Viscosity at 5 °C in 10^9 poises						
Original	1.22	1.00	0.87	5.30	5.56	3.12
90	9.77	8.74	11.80	17.92	10.63	2.52
100	13.33	16.20	17.85	28.63	11.17	7.85
110	25.70	22.90	32.60	34.71	21.21	11.26
Carbonyl Ratio						
Original	0.3083	0.3214	-	0.3044	0.3874	0.2209
90	0.4502	0.4431	-	0.4120	0.5442	0.3840
100	0.4896	0.4582	-	0.4354	0.5229	0.4678
110	0.5759	0.5437	-	0.4958	0.5828	0.5129

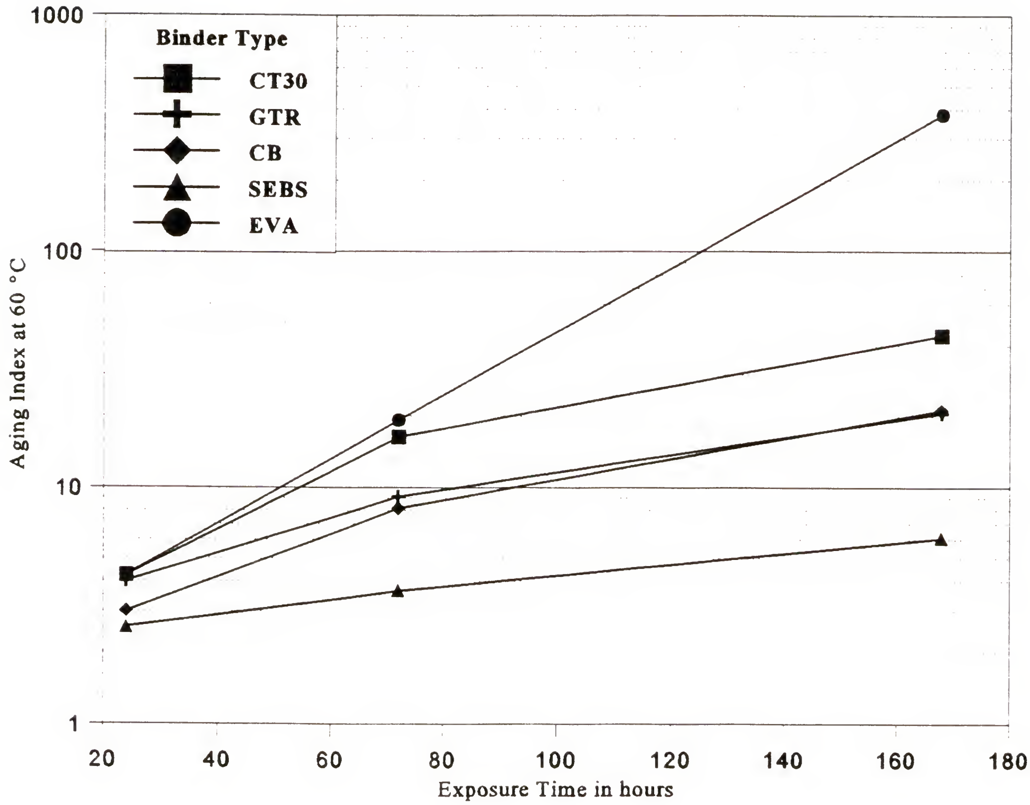
Note:

See Table 3-1 for the meaning of codes.

longer reaction time and PAV process provides higher oxygen content through pressurized air.

The effects of the CTO processes on the aging index at 60 °C of the different modifiers are shown in Figure 6-2. The same statistical model as described in section 5.2 was used to analyze the logarithm of aging index at 60 °C. Due to the significant effect of interaction of the two main factors, the Duncan's Multiple Range test was performed at separate aging levels. The summary of results of statistical analyses is shown in Table 6-3. As indicated in Figure 6-2 and Table 6-3, the EVA modified asphalt showed a high aging index, particularly when the process time is long, as in the case of 168-hour California Tilt Oven process.

Based on the results of tests on the CTO residues, all three modified asphalts with the exception of the EVA modified asphalt, show a lower aging potential in terms of lower aging indices at 60 °C as compared with that of conventional asphalts. Carbon black and fine ground tire rubber modified binders used in this study exhibit similar aging indices. The SEBS modified asphalt exhibits a very low aging index, which might be attributed to the slower movement of the binders in the flasks during the rolling process of the CTO due to its high initial viscosity. This does not necessarily mean that the SEBS modified asphalt will have a lower thermal cracking potential than the EVA modified asphalt or the control AC-30. As long as the aged residues have low enough viscosity to prevent the built-up of high thermal stresses, an asphalt with low initial viscosity could be allowed to be aged to a high degree. As shown in Figure 6-3, after a 72-hour exposure in the CTO process, all four modified asphalts show a lower viscosity at 5 °C, as compared with their



Note: See Table 3-1 for the meaning of codes.

Figure 6-2 The Effect of California Tilt Oven Process on the Aging Indices based on the Viscosity at 60 °C of Modified Asphalts

Table 6-3 Results of ANOVA and Duncan's Multiple Range Test on the Logarithm of Aging Index at 60 °C of Modified Asphalts Aged by the CTO Processes

Dependent Variable: % penetration retained

Source	DF	Sum of Squares	Mean Squares	F Value	Pr > F
Model	14	9.18783550	0.65627382	60.95	0.0001
Error	15	0.16151730	0.01076782		
Corrected Total	29	9.34935079			

R-Square	C.V.	Root MSE	Overall Mean
0.982724	10.20505	0.103768	1.01683102

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Asphalt (τ)	4	2.82970444	0.70742611	65.70	0.0001
Method (β)	2	4.88079555	2.44039778	226.64	0.0001
Interaction ($\tau\beta$)	8	1.47733350	0.18466669	17.15	0.0001

Duncan Grouping at β = C24

Grouping	Mean	N	Asphalt	Aging Index
A	0.6304	2	EVA	4.27
A	0.6263	2	CT30	4.23
A	0.6042	2	GTR	4.02
A	0.4785	2	CB	3.01
A	0.4082	2	SEBS	2.56

Duncan Grouping at β = C72

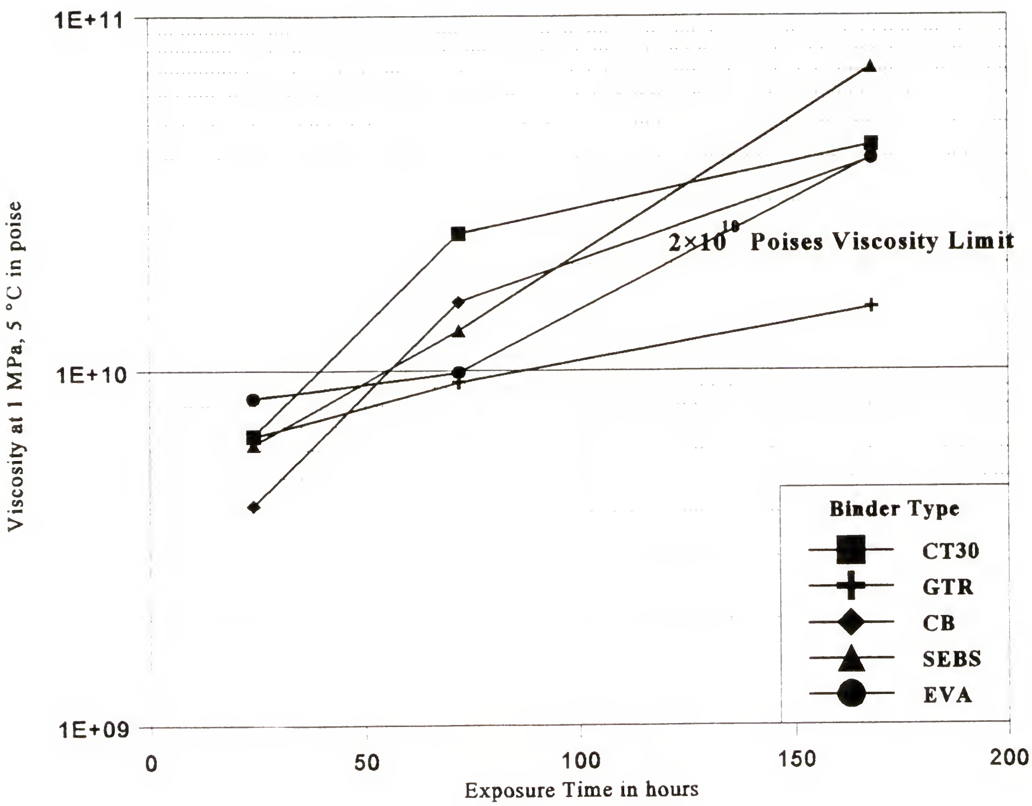
Grouping	Mean	N	Asphalt	Aging Index
A	1.2856	2	EVA	19.30
A	1.2146	2	CT30	16.39
B	0.9590	2	GTR	9.10
B	0.9106	2	CB	8.14
C	0.5623	2	SEBS	3.65

Duncan Grouping at β = C168

Grouping	Mean	N	Asphalt	Aging Index
A	2.5800	2	EVA	380.19
B	1.6470	2	CT30	44.36
C	1.3280	2	GTR	21.28
C	1.3149	2	CB	20.65
D	0.7860	2	SEBS	6.11

Note:

Means with the same letter are not significantly different at α = 0.05.
See Table 3-1 and Table 3-2 for the meaning of codes.

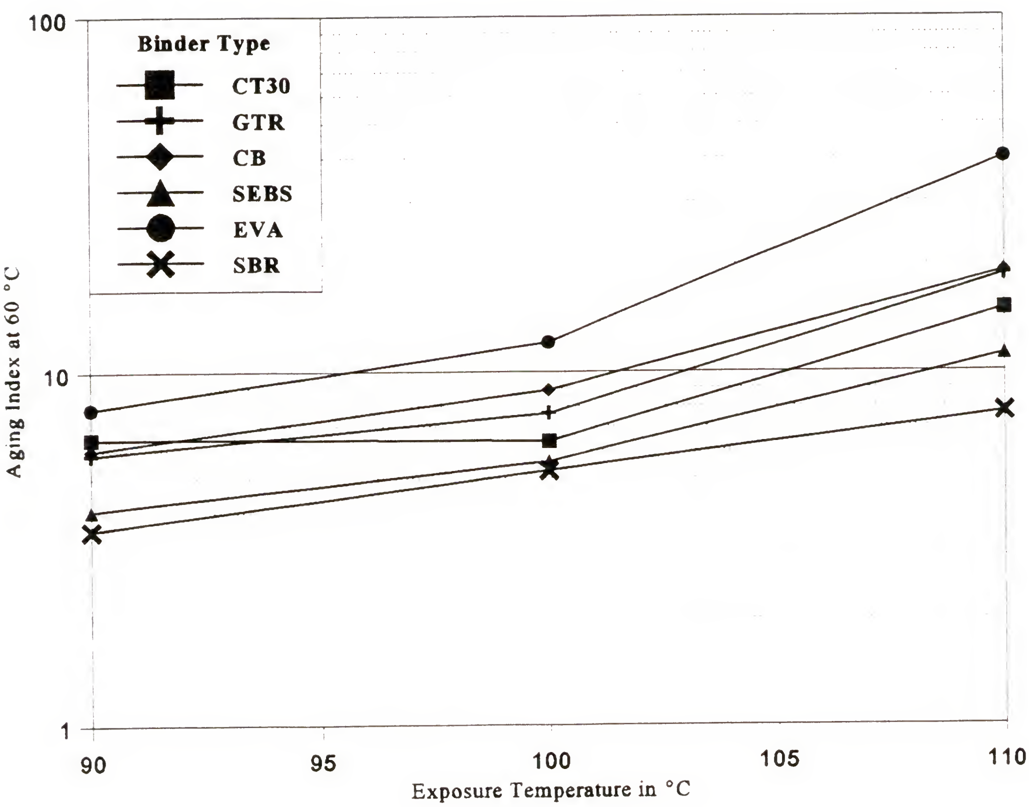


Note: See Table 3-1 for the meaning of codes.

Figure 6-3 The Effect of California Tilt Oven Process on the Constant Stress (1MPa) Viscosity at 5 °C of Modified Asphalts

base AC-30. However, after a 168-hour exposure in the CTO, only the fine ground tire rubber modified asphalt shows a significantly lower viscosity at 5 °C.

The effects of the PAV processes of the different modified binders on the aging index at 60 °C are plotted in Figure 6-4, and the summary of the results of statistical analyses is shown in Table 6-4. In the PAV process at 90 °C, only the SBR and SEBS modified asphalts show significantly less severe aging than the control AC-30 in terms of aging index at 60 °C, as indicated in Figure 6-4 and Table 6-4. After the PAV process at 100 °C, the carbon black and EVA modified asphalt show more severe aging than the control AC-30. Although SBR and SEBS modified asphalts show less aging after the PAV process at 100 °C, the difference is statistically insignificant. After the PAV process at 110 °C, EVA, carbon black and ground tire rubber modified asphalts show higher aging index at 60 °C than the control AC-30. On the other hand, SBR and SEBS modified asphalts exhibit lower aging index at 60 °C as compared with their base AC-30. The SBR modified asphalt exhibits a substantially lower viscosity at 5 °C and the SEBS modified asphalt show a substantially higher viscosity at 5 °C as indicated in Figure 6-5. If the PAV processes could simulate long-term aging in the field, these results would indicate that the SBR modified asphalt would probably have a lower thermal cracking potential, while the SEBS modified asphalt would have a higher thermal cracking potential than that of the base asphalt. This observation may not be conclusive since there was great variability in the results of the Schweyer rheometer tests on the SBR modified asphalts. This great variability of the test results might be due to the high compressibility of the



Note: See Table 3-1 for the meaning of codes.

Figure 6-4 The Effect of Pressure Aging Vessel Process on the Aging Indices based on the Viscosity at 60 °C of Modified Asphalts

Table 6-4 Results of ANOVA and Duncan's Multiple Range Test on the Logarithm of Aging Index at 60 °C of Modified Asphalts Aged by the PAV Processes

Dependent Variable: % penetration retained

Source	DF	Sum of Squares	Mean Squares	F Value	Pr > F
Model	17	2.38259903	0.14015288	82.19	0.0001
Error	18	0.03042661	0.00169037		
Corrected Total	35	2.41302565			

R-Square	C.V.	Root MSE	Overall Mean
0.987391	4.396256	0.041114	0.93520656

Source	DF	Anova SS	Mean Square	F Value	Pr > F
Asphalt (τ)	5	0.81582206	0.16316441	96.53	0.0001
Method (β)	2	1.43962336	0.71981168	425.83	0.0001
Interaction ($\tau\beta$)	10	0.12715361	0.01271536	7.52	0.0001

Duncan Grouping at β = P90

Grouping		Mean	N	Asphalt	Aging Index
	A	0.8959	2	EVA	7.87
B	A	0.8116	2	CT30	6.48
B		0.7774	2	CB	5.99
B		0.7649	2	GTR	5.82
	C	0.6074	2	SEBS	4.05
	C	0.5527	2	SBR	3.57

Duncan Grouping at β = C72

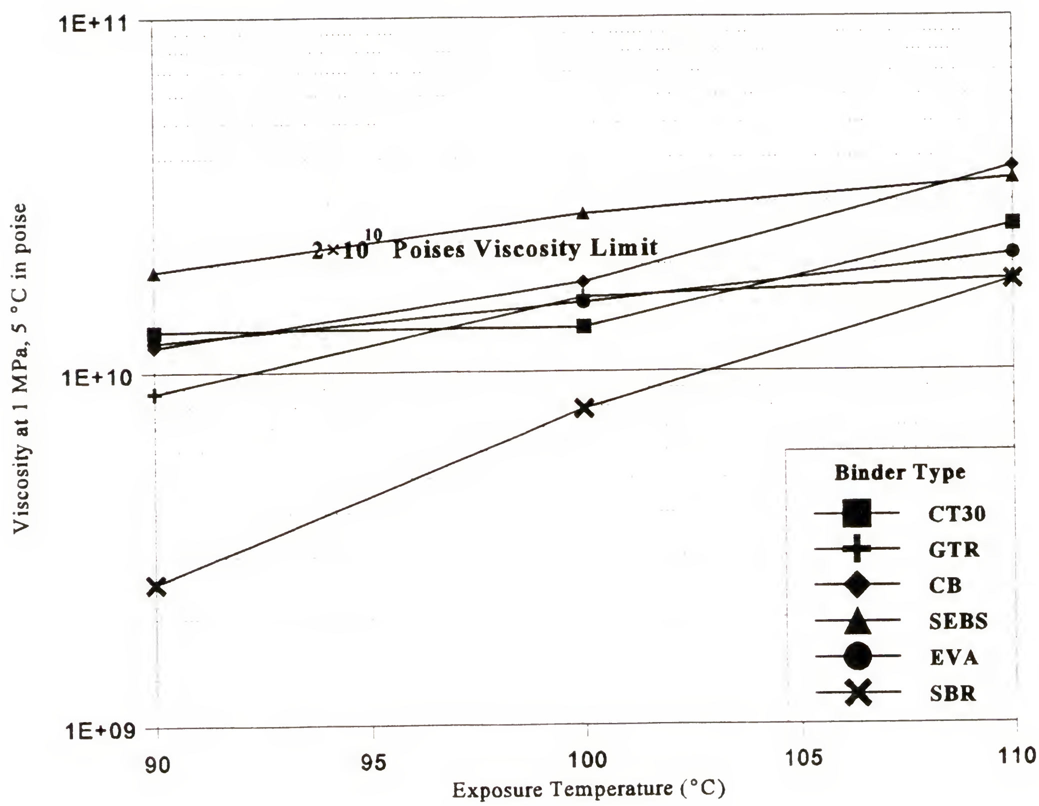
Grouping		Mean	N	Asphalt	Aging Index
	A	1.0824	2	EVA	12.09
	B	0.9484	2	CB	8.88
C	B	0.8825	2	GTR	7.63
C	D	0.8028	2	CT30	6.35
	D	0.7466	2	SEBS	5.58
	D	0.7202	2	SBR	5.25

Duncan Grouping at β = C168

Grouping	Mean	N	Asphalt	Aging Index
A	1.6024	2	EVA	40.03
B	1.2785	2	CB	18.99
B	1.2707	2	GTR	18.65
C	1.1740	2	CT30	14.93
D	1.0477	2	SEBS	11.16
D	0.8848	2	SBR	7.67

Note:

Means with the same letter are not significantly different at $\alpha = 0.05$.
See Table 3-1 and Table 3-2 for the meaning of codes.



Note: See Table 3-1 for the meaning of codes.

Figure 6-5 The Effect of Pressure Aging Vessel Process on the Constant Stress (1MPa) Viscosity at 5 °C of Modified Asphalts

SBR modified asphalts, which makes the basic assumptions of the Schweyer rheometer test invalid.

The infrared spectral analysis on the modified binders show that the EVA modified asphalts have higher carbonyl ratio than the control asphalt both in the unaged state and CTO or PAV aged residues. On the other hand, the SBR modified asphalts exhibit a significantly lower carbonyl ratio than the control asphalt in the unaged state shown in Appendix B. The carbonyl functional group of an asphalt binder is very likely to be changed to some extend by the addition of these two modifiers. When the carbonyl ratio index was used to represent the oxidation rate, the EVA and GTR modified asphalts show similar oxidation rates to the control asphalt and the SBR modified asphalt show a significant higher oxidation rate than the control asphalt. The SEBS modified asphalts generally show a lower oxidation rate than the control asphalt.

Based on the penetration and viscosity measurements, $PVN'_{(25\text{-}60)}$ and $VTS\ (60\text{-}5)$, which are conventionally used as the temperature susceptibility parameters, were calculated and displayed in Table 6-5. All five modifiers reduced the temperature susceptibility of the asphalt before aging as represented by higher PVN' and lower VTS value in Table 6-5. As the binders were aged , their PVN' values increase and their VTS values decrease with increasing age hardening. This observation applies to both the unmodified asphalts as well as the modified asphalts.

6.4 Use of Brookfield Rheometer for Measuring Viscosity at 60 °C

The benefit of using Brookfield Rheometer instead of capillary tube is the convenience of sample preparation and cleaning of the equipment after the test. The

Table 6-5 Temperature Susceptibility Parameter, $PVN'_{(25\text{-}60)}$ and $VTS(60\text{-}5)$ of the Modified Binders and their Residues Aged by CTO and PAV Processes

Aging Process	$PVN'_{(25\text{-}60)}$					
	CT30	GTR	CB	SEBS	EVA	SBR
Original	-0.57	-0.16	-0.34	0.21	-0.55	-
C24	-0.11	0.39	-0.17	0.76	-0.07	-
C72	0.43	0.54	0.14	0.67	0.84	-
C168	0.83	1.03	0.61	0.94	2.66	-
P90	-0.05	0.49	0.17	1.44	1.56	1.08
P100	-0.12	0.60	0.38	1.51	0.83	1.49
P110	0.54	0.88	0.70	1.85	1.72	1.63
	$VTS(60\text{-}5)$					
Original	3.92	3.57	3.65	3.36	4.02	3.72
C24	3.68	3.42	3.54	3.08	3.52	-
C72	3.43	3.19	3.43	3.10	3.01	-
C168	3.19	3.84	3.26	3.24	2.32	-
P90	3.63	3.34	3.48	3.10	3.34	3.18
P100	3.60	3.36	3.42	3.08	3.19	3.27
P110	3.45	3.19	3.26	2.89	2.91	3.21

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.
$PVN'_{(25\text{-}60)}$ and $VTS(60\text{-}5)$ are computed by Equation 7 and Equation 5, respectively.

asphalt residues (both conventional and modified) aged by the PAV procedures were further tested by using the Brookfield rheometer for the viscosities at 60 °C. The viscosities at a shear rate of 1 sec^{-1} ($\eta_{1.0}$) obtained in the Brookfield rheometer at 60 °C are listed in Appendix C along with their corresponding absolute viscosity.

A comparison of $\eta_{1.0}$ and absolute viscosity is displayed in Figure 6-6. It can be observed in Figure 6-6 that $\eta_{1.0}$ is generally larger than the absolute viscosity obtained from capillary tube in the lower viscosity range (≤ 10000 poises), while the reverse is true in the high viscosity range (≥ 10000 poises). This is due to the fact that absolute viscosity is generally performed at a shear rate higher than 1.0 sec^{-1} in the low viscosity range and smaller than 1.0 sec^{-1} in the high viscosity range. And most asphalt binders exhibit a non-Newtonian behavior at 60 °C as observed in the Brookfield rheometer tests.

A linear regression analysis was performed on the logarithm transformed data. The following equation was obtained and used for the calculation of absolute viscosity from $\eta_{1.0}$.

$$AbsV = 10^{-0.23815 + 1.065412 \times \log(\eta_{1.0})} \qquad (13)$$

Equation 13 was based on a total of 84 data points which represent a degree of freedom of 82. The R-Square of the linear model is 0.966438. It is believed that η 1.0 can be used in place of the absolute viscosity.

6.5 Comparison of TFOT and RTFOT in the Process of PAV

A testing program for investigating the possible difference between a TFOT and a RTFOT treatment of the asphalt samples in the PAV process was conducted. The new

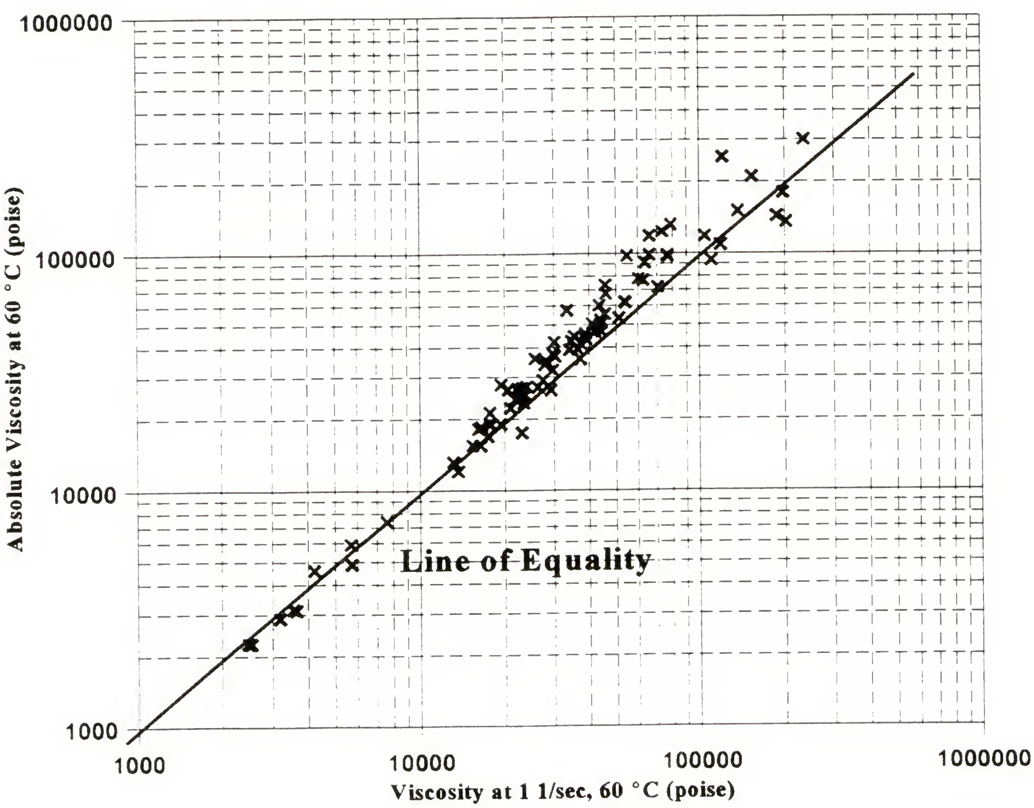


Figure 6-6 The Comparison of Brookfield Viscosity at Shear Rate of 1 sec^{-1} with Capillary Tube Viscosity at 60 °C

PAV apparatus at the Materials Office of Florida Department of Transportation was used in this testing program. The Brookfield rheometer was used to measure the viscosity at 60 °C of the binders before and after the different aging processes. The aging index at 60 °C was used as a parameter to evaluate the aging severity of the different processes.

It was found that the SBR modified binder flowed out of the bottles in the RTFOT process, and thus the RTFOT was not run on the SBR modified binder. These was no visible difference in the amount of air bubbles formed on the surface between those residues aged by TFOT+PAV and RTFOT+PAV. Appendix D lists the results of the Brookfield viscosity tests on the different binders which were aged by different combinations of RTFOT/TFOT and PAV processes. The computed aging indices of the different aged binders, and their relative ranking in terms of aging severity are displayed in Table 6-6. The data show that the AM asphalts generally age more than the other asphalts and the relatively rankings between RTFOT+PAV and TFOT +PAV generally aggree with each other. The conventional CT30 and the modified CT30 binders show lower hardening potential than the other four conventional asphalts.

Figure 6-7 shows a plot of the aging indices of the residues after the TFOT+PAV processes versus those after the RTFOT+PAV processes. It can be seen that the RTFOT+PAV process produced consistently more severe aging on the binders. This is probably due to the formation of skin in the TFOT process, which retards the further aging of the asphalt samples. For example, formation of skin in CT30 (with a high volatile loss) in the TFOT process might cause it to have a lower aging severity ranking of 6.

Table 6-6 Aging Indices at 60 °C of the Residues aged by different combinations of RTFOT/TFOT and PAV processes (Brookfield Rheometer Data)

Aging Process	Asphalt Type							
	CT30	AM30	AM20	MA30	MA20	GTR	CB	SBR
RTFOT	2.57	3.38	3.24	3.16	3.16	2.99	3.38	-
Ranking	7	1.5	3	4.5	4.5	6	1.5	-
TFOT	2.02	3.20	3.06	2.32	2.46	1.97	2.28	2.89
Ranking	7	1	2	5	4	8	6	3
RTFOT+PAV 90 °C	6.30	9.20	9.37	7.86	8.29	6.71	7.48	-
Ranking	7	2	1	4	3	6	5	-
RTFOT+PAV100 °C	9.86	12.90	14.30	11.46	12.47	9.36	11.76	-
Ranking	6	2	1	5	3	7	4	-
RTFOT+PAV110 °C	20.81	39.69	35.51	20.79	22.13	20.06	19.28	-
Ranking	4	1	2	5	3	6	7	-
TFOT+PAV 90 °C	5.86	7.85	7.99	6.76	7.21	5.27	6.47	4.75
Ranking	6	2	1	4	3	7	5	8
TFOT+PAV100 °C	9.13	13.22	13.27	11.21	11.94	7.83	10.78	5.88
Ranking	6	2	1	4	3	7	5	8
TFOT+PAV110 °C	17.64	30.62	27.31	20.11	17.80	13.07	19.93	6.83
Ranking	6	1	2	3	5	7	4	8

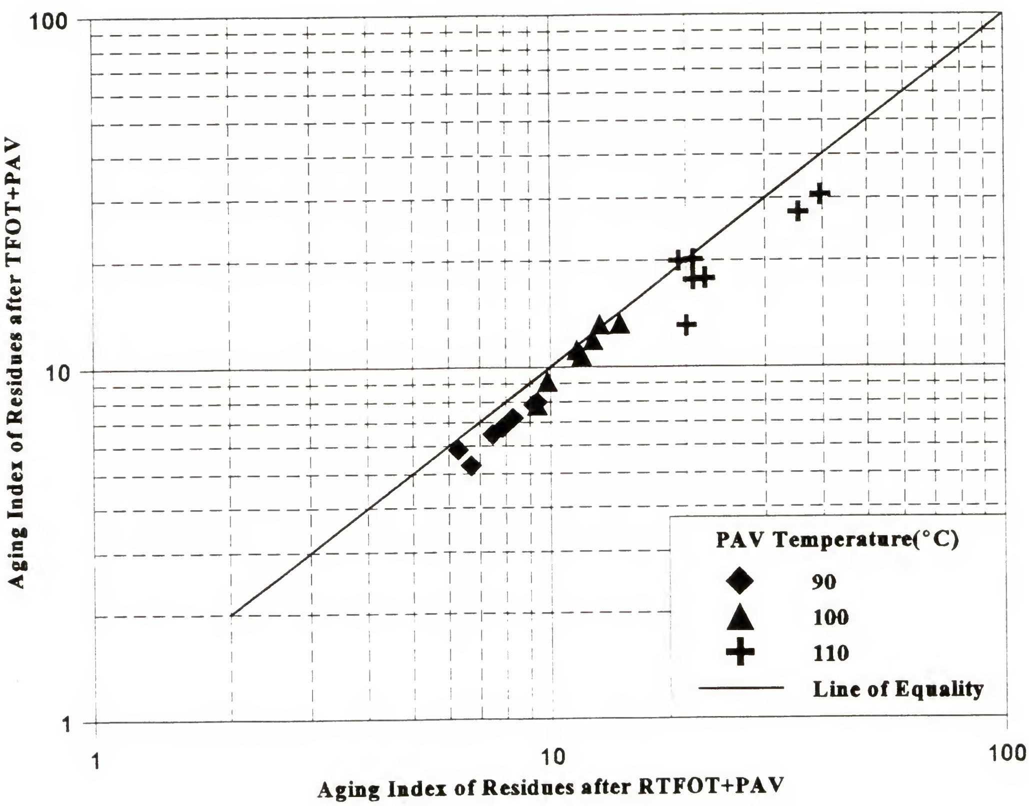


Figure 6-7 Comparison of Aging Indices at 60 °C of Residues after TFOT+PAV and those after RTFOT+PAV Processes

Without the skin formation in the RTFOT aged samples, the severity ranking of the CT30 asphalt rose to 4 in the case of RTFOT+PAV at 110 °C.

It is interesting to note that, while the SBR modified asphalt shows a relatively high hardening potential in the TFOT process, it shows a relatively low hardening potential after additional aging in the PAV process as shown in Table 6-5.

6.6 Summary of Findings

Five different modifiers including fine ground tire rubber, carbon black, SEBS, EVA, and SBR, have been investigated in this study for their effects on the aging characteristics of the modified asphalt. A rotational viscometer, Brookfield rheometer, was used to measure the viscosity of asphalt binders at 60 °C. A testing program for investigating the possible difference between a TFOT and a RTFOT treatment of the asphalt samples before the PAV process was also conducted. These research efforts result in the following conclusions:

(1) Some modified binders might become inhomogeneous in consistency to some degree if care is not taken to ensure homogeneous blending of the modifiers and the asphalt.

(2) Most of the modified asphalts, except EVA modified asphalt, show less aging in the CTO process than the control asphalt in terms of aging index at 60 °C. All of the modified asphalts show a lower viscosity at 5 °C than the control asphalt after a 72-hour CTO exposure. However, after a 168-hour CTO exposure, only the ground tire rubber modified asphalt exhibit a lower viscosity at 5 °C than the control asphalt.

(3) In terms of the aging index at 60 °C, the effect of modifiers on reducing the aging severity of asphalts in the PAV process is different at different process temperatures. Aftert the PAV process at 90 °C, SEBS and SBR modified asphalts exhibit lower aging index at 60 °C than the control asphalt. When the process temperature was increased to 100 °C, no substantial reduction of aging index was found for any of the five modified asphalts as compared with the control asphalt. The fine ground tire rubber, SEBS and SBR modified asphalts exhibit lower aging index than the control asphalt at the process temperature of 110 °C.

(4) The Brookfield rheometer can be used to measure the viscosity of asphalt binder at 60 °C. This testing apparatus is much easier to use than the conventional capillary tube. An equation (Equation 14) has been established through linear regression analysis to convert the Brookfield viscosity ($\eta_{1.0}$) to the absolute viscosity.

(5) The possibility of skin-formation in some asphalts aged in the TFOT+PAV process might cause a lower aging effect by TFOT+PAV process than those by the RTFOT+PAV process.

CHAPTER 7
INVESTIGATION OF AGING OF ASPHALT MIXTURES

7.1 Introduction

A testing program on the aging of asphalt mixtures was performed to correlate asphalt aging in binder-only state with that in the mixture state. The five conventional asphalts used in the testing program on asphalt binders as described in Chapter 5 were blended with an aggregate with a fixed gradation and at a fixed asphalt content in the laboratory to produce mixtures complying with the Florida DOT S-I mix specification. Some mixtures were subjected to a forced-draft oven and the UV chamber at 60 °C for 28 days. The other mixtures were subjected to the SHRP proposed short term oven aging (STOA) and long term oven aging (LTOA) processes as described earlier in Figure 3-9. The asphalt binders were recovered from the aged mixtures by using the reflux/Rotavapor 2 procedure as described in Chapter 4. Brookfield Rheometer tests were performed on the recovered binders to measure their viscosities at 60 °C. Marshall samples, which were made in the previous study [17] and had been aged under natural sunlight up to four years, were also tested. The asphalt binders were recovered from these Marshall samples at the ages of two and four years. Viscosity tests were performed on the recovered binders and the data were analyzed. An age hardening model was developed and

evaluated by using the absolute viscosity data obtained from this study and those from some paving projects.

7.2 Laboratory Aging on Mixtures

Table 7-1 displays the results of tests on recovered binders from the loose mixtures aged in the UV chamber and the forced-draft oven at 60 °C for 28 days. The $\eta_{1.0}$ obtained in the Brookkfield Rheometer tests were converted, according to Equation 14, to the equivalent absolute viscosities for a consistent comparison of data. The AM asphalts exhibit higher aging indices than the other asphalts as shown in Table 7-1. The MA asphalts show lower aging indices than the other asphalts in the forced-draft oven test. These results are consistent with those obtained in the binder-only aging methods.

The aging effect of the UV chamber on loose mixtures is consistently more severe than that of the forced-draft oven as shown in Figure 7-1. The average aging indices at 60 °C of the recovered binders from the loose mixtures are 8.17 and 10.76, for the forced-draft oven and UV chamber aging, respectively. In the log-log plot of viscosity versus absolute temperature, these values represent parallel shifts ($\Delta\beta$ in Equation 9) of 0.9124 and 1.0318, which are equivalent to those of the 100 °C PAV and 15 hour TFOT as listed in Table 5-7, respectively.

Table 7-2 displays the relative rankings of aging severity of residues including those aged in the loose-mixture states and those aged in the binder-only states. The five asphalts were ranked from 1 to 5 according to their aging indices, with 1 being the highest and 5 being the lowest. Two methods, TFOT (TS) and high temperature TFOT (TH), aged the five asphalts in the same severity order as did the 60 °C force-draft oven on the

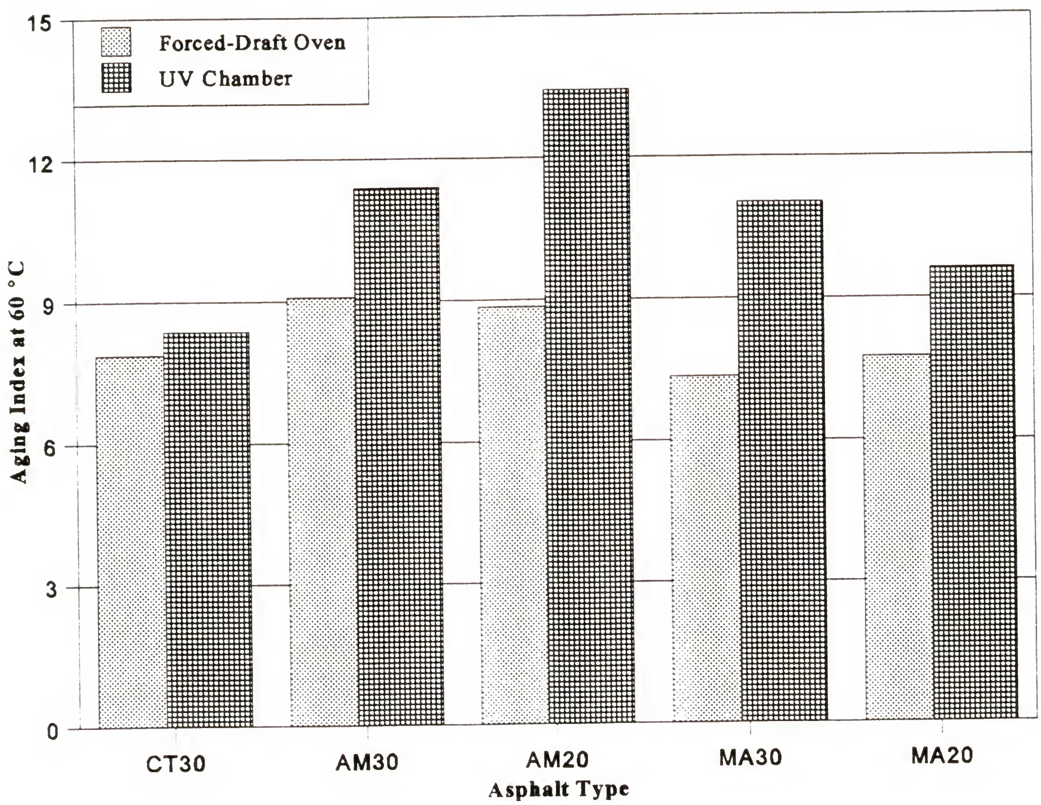
Table 7-1 Results of Tests on Recovered Binders from the Loose Mixtures Aged in the UV Chamber and Forced-Draft Oven

Asphalt Type	CT30	AM30	AM20	MA30	MA20
Original, Absolute viscosity in poise	2883	3146	2246	3108	2248
Forced-Draft Oven at 60 °C for 28 days					
$\eta_{1.0}$ in poise (#1)	22509	22016	18454	20580	16492
$\eta_{1.0}$ in poise (#2)	18517	28891	17733	20638	15496
$\eta_{1.0}$ in poise (Average)	20513	25454	18094	20609	15994
Converted absolute viscosity in poise	22695	28562	19855	22808	17410
Aging Index at 60 °C	7.87	9.08	8.84	7.34	7.74
UV Chamber at 60 °C for 28 days					
$\eta_{1.0}$ in poise (#1)	24288	31969	25920	29085	20220
$\eta_{1.0}$ in poise (#2)	19132	30950	27672	31268	18966
$\eta_{1.0}$ in poise (Average)	21710	31460	26796	30177	19593
Converted absolute viscosity in poise	24109	35794	30165	34241	21612
Aging Index at 60 °C	8.36	11.38	13.43	11.02	9.61

Note:

See Table 3-1 for the meaning of codes.

$\eta_{1.0}$ was converted to absolute viscosity according to Equation 13 in Chapter 6.



Note: See Table 3-1 for the meaning of codes.

Figure 7-1 Aging Index at 60 °C of Recovered Binders from Loose Mixtures Aged in Forced-Draft Oven and UV Chamber at 60 °C for 28 days

Table 7-2 The Relative Ranking of Aging Severity of Residues of the Five Asphalts aged by Different Laboratory Aging Processes

Laboratory Aging Process	Relative Ranking of Aging Severity				
	CT30	AM30	AM20	MA30	MA20
Mixture, FD	3	1	2	5	4
Mixture, UV	5	2	1	3	4
TL	1	2	3	4	5
TS	3	1	2	5	4
TH	3	1	2	5	4
TLM	3	1	2	4	5
TSM	3	1	2	4	5
THM	3	1	2	4	5
TF10	3	2	1	5	4
TF15	3	1	2	4	5
UV7	5	3	1	2	4
UV14	4	5	1	2	3
UV28	5	4	1	2	3
C24	4	5	3	2	1
C72	3	4	1	5	2
C168	2	4	1	5	3
P90	5	1	2	3	4
P100	5	2	1	3	4
P110	5	1	2	4	3

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.
Mixture, FD: Loose mixture aged in the forced-draft oven at 60 °C for 28 days.
Mixture, UV: Loose mixture aged in the UV chamber at 60 °C for 28 days.

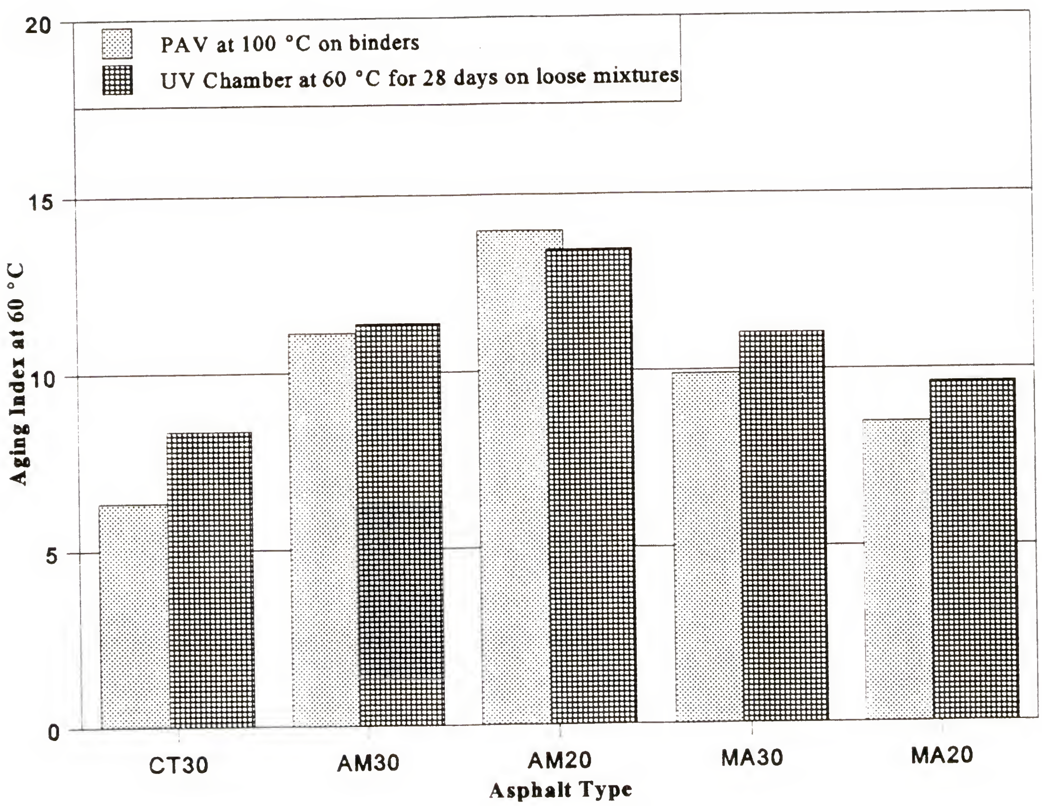
loose mixtures for 28 days. The 100 °C PAV aged the five asphalts in the same order as did the 60 °C UV chamber on the loose mixtures for 28 days.

The extended TFOT and PAVs could differentiate the aging potential of different asphalts very well as shown in Table 7-2 with consistent rankings similar to those in the mixtures. On the other hand, the California Tilt Oven seems to have a bias interpretation of the aging potential of asphalts. The PAV process at 100 °C can simulate the aging effects of 60 °C UV chamber on the loose mixtures for 28 days, not only with the same relative ranking of aging potential of different asphalts but also with similar aging severity in terms of aging index at 60 °C. Figure 7-2 shows the comparison of the aging effects of these two procedures in terms of the aging index at 60 °C.

7.3 SHRP Proposed Aging Procedures on Mixtures

Laboratory-mixed mixtures were subjected to a 135 °C forced-draft oven for four hours with stirring at each hour interval according to the SHRP proposed short term oven aging (STOA) on the mixtures. Some STOA-aged mixtures were compacted and subjected to an 85 °C forced draft oven for five days, according to the SHRP proposed long term oven aging (LTOA) procedures. To achieve a higher degree of aging through similar method, some STOA-aged mixtures were subjected, in their loose state, to the 85 °C forced draft oven for five days. Asphalt binders were recovered from these mixtures by using the reflux/Rotavapor 2 method and Brookfield Rheometer tests were performed on these recovered binders.

Table 7-3 displays the test results on residues recovered from the mixtures, which were aged by the SHRP proposed procedures. The average aging indices (60 °C)



Note: See Table 3-1 for the meaning of codes.

Figure 7-2 Comparison of Aging Indices at 60 °C of Residues Aged by the PAV at 100 °C with those Recovered from Loose Mixtures Aged in the UV Chamber at 60 °C for 28 days

Table 7-3 Results of Tests on Recovered Binders from the Mixtures Aged in the SHRP Proposed Procedures

Asphalt Type	CT30	AM30	AM20	MA30	MA20
Original, Absolute viscosity in poise	2883	3146	2246	3108	2248
STOA					
$\eta_{1.0}$ in poise	13839	20824	12217	25883	16644
Converted absolute viscosity in poise	14922	22426	13066	29076	18165
Aging Index at 60 °C	5.18	7.13	5.82	9.36	8.08
Ranking	5	3	4	1	2
LTOA					
$\eta_{1.0}$ in poise	26218	44036	26886	28644	21100
Converted absolute viscosity in poise	29477	51218	30278	32391	23388
Aging Index at 60 °C	10.22	16.28	13.48	10.42	10.40
Ranking	5	1	2	3	4
STOA and 85 °C, loose state, 5 days					
$\eta_{1.0}$ in poise	31841	57446	31908	37190	20288
Converted absolute viscosity in poise	36257	6786	3338	42780	22430
Aging index at 60 °C	12.58	21.61	16.18	13.76	13.76
Ranking	4	1	2	3	5

Note:

See Table 3-1 for the meaning of codes.

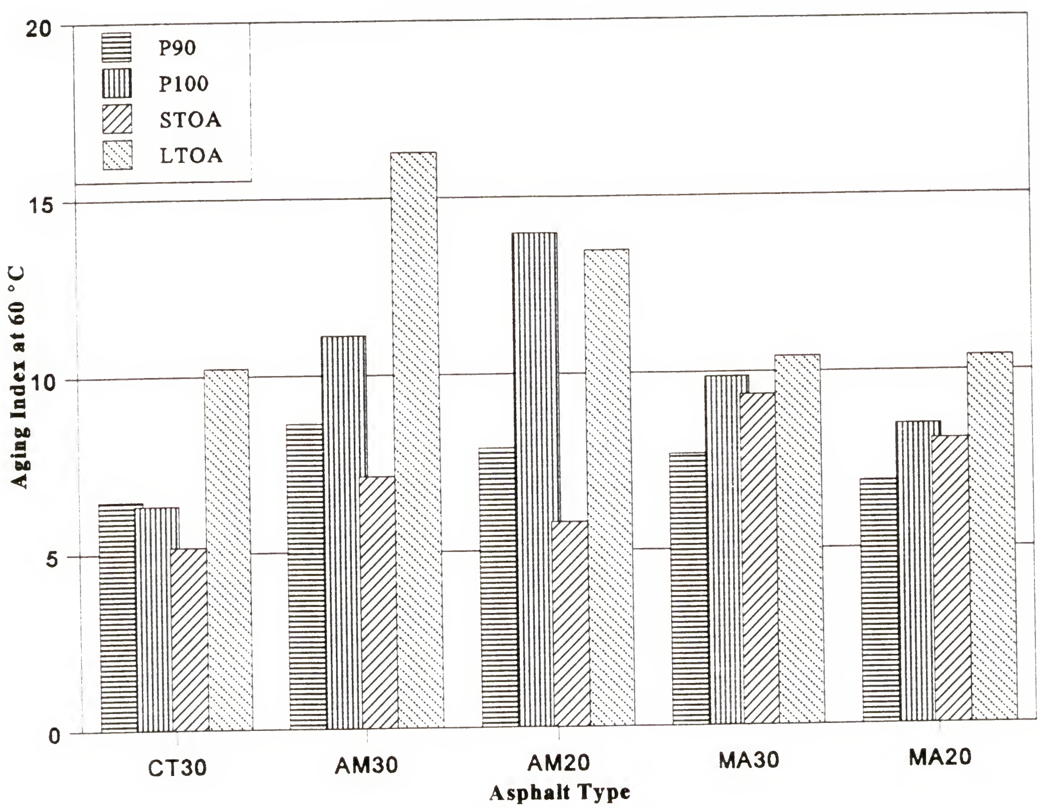
$\eta_{1.0}$ was converted to absolute viscosity according to Equation 13 in Chapter 6.

produced by the STOA and the LTOA procedures are 7.11 and 12.16, respectively. In the log-log plot of viscosity versus absolute temperature, these values represent the amount of parallel shifts ($\Delta\beta$ in Equation 9) of 0.8519 and 1.0849. When compared with the average aging severity of different binder-aging methods as listed in Table 5-7, the STOA and LTOA produced aging indices close to those produced by the 90 °C-PAV and the 100 °C-PAV, respectively. The aging indices at 60 °C of the residues aged by P90, P100, STOA, and LTOA are plotted together in Figure 7-3. It is evident that the STOA is too severe to simulate the short-term aging of asphalt binders. On the other hand, an average aging index of 15.58 was produced when the STOA-aged mixtures were further aged, in their loose states, in an 85 °C forced-draft oven for five days. This is equivalent to an $\Delta\beta$ value of 1.1925, which is close to that of the California Tilt Oven for 72 hours.

The relative severity ranking of STOA-aged residues suggests that the MA asphalts have a higher aging potential than the other asphalts, which is contrary to the results obtained by most of the methods investigated in this study. Nevertheless, the rankings of LTOA and loose state LTOA aged residues are consistent with those of most aging methods. The five asphalts after aging by the LTOA process have the same relative aging severity order as that after the 90 °C-PAV, as shown in Figure 7-3.

7.4 Marshall Samples Aged under Natural Sunlight

Marshall samples which were made in a previous study and aged under natural sunlight up to four years were evaluated in this study. Five different AC-30 binders, which were denoted as BF30, MA30, MT30, CT30, and BJ30A, were used to make these samples according to the specification of FDOT S-I mix. At the age of four years, all



Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Figure 7-3 Comparison of Aging Indices at 60 °C Produced by the Processes of P90, P100, STOA, and LTOA

BJ30A samples exhibited visible cracks on the surface and one of the four MT30 samples exhibited a minor surface crack. Asphalt binders were recovered from these samples at the ages of two and four years. The Brookfield Rheometer tests were performed on the recovered residues.

Table 7-4 displays test results obtained in this study, along with those obtained in the previous research [17]. The viscosities at 60 °C are plotted in Figure 7-4 versus the exposure time (day). The data points at the age of 0 day are treated as at the age of one day in order to be plotted in a logarithm scale. It is noticed that the rates of age hardening seem to keep increasing with exposure time. This is an abnormal phenomena considering the general growth curve of most chemical reactions, in which the reaction rate is reduced with time.

Table 7-5 lists the aging index at 60 °C and relative severity ranking of residues recovered from Marshall samples. Different asphalts show different aging severities under the same environment as shown by the wide range of aging indices at the same age in Table 7-5. BF30 and MA30 were ranked consistently at all ages as 5 and 4, respectively. These two asphalts show a lower aging potential under natural sunlight for four years. The cracked BJ30A samples were ranked as 2, 2, and 1 at the ages of one, two, and four years, respectively. The MT30 samples were all ranked as 3 at the ages of one, two, and four years. Since the MT30 and BJ30A samples exhibited cracks, the MT30 and BJ30A asphalts should be ranked with the CT30 asphalt as among the most severe aging asphalts under Florida's condition.

Table 7-4 Results of Tests on Recovered Binders from the Marshall Samples Aged under Natural Sunlight

Age (day)	Absolute Viscosity at 60 °C in poise				
	BF30	MA30	MT30	CT30	BJ30A
Original	4130	3202	3410	2890	3335
TFOT	7924	6958	8472	6996	7848
0	7010	6491	9424	10567	10777
90	11310	10313	20225	20239	14959
180	16074	14171	22904	21931	20353
360	13525	14246	21446	26589	26346
720	21372	20874	35395	46976	35414
1440 ($\eta_{1.0}$)	64007	57116	81070	113064	149697
1440 Converted	76289	67570	98132	139869	188618

Note:

Data up to 360 days were obtained from Reference 17.

Asphalt Type: [17]

BF30: Belcher FT. Lauderdale AC-30.

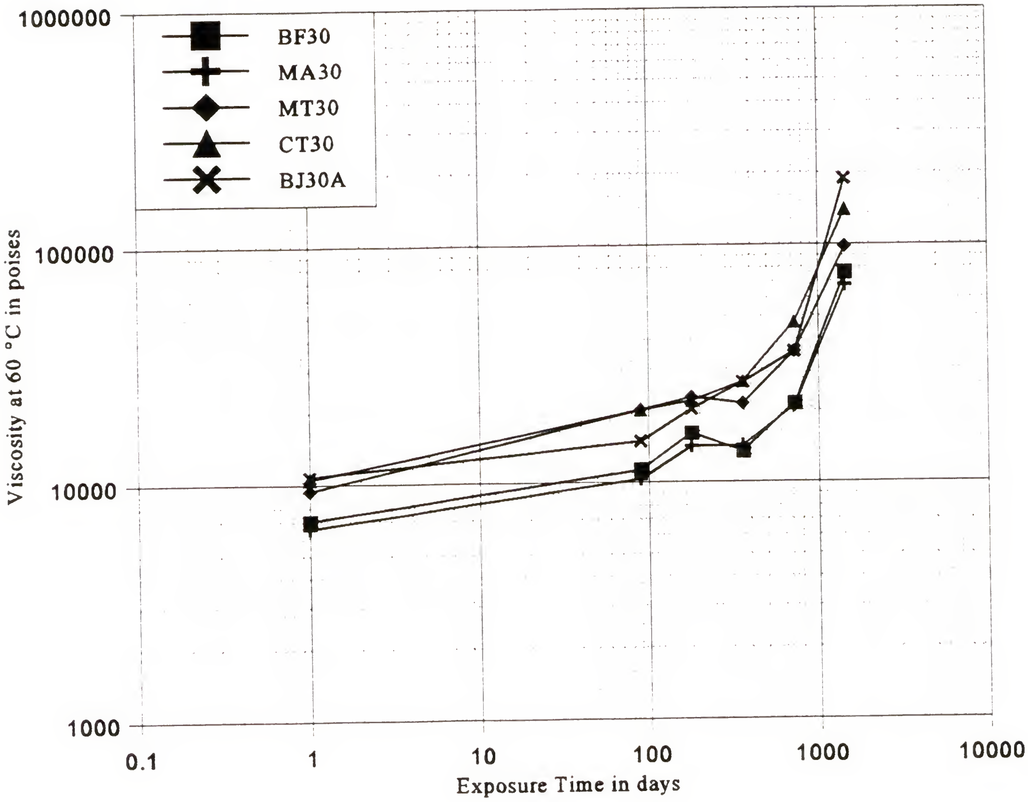
MA30: Mariani AC-30.

MT30: Marathon Tampa AC-30.

CT30: Chevron Tampa AC-30.

BJ30A: Belcher JAX AC-30 Anti-strip.

$\eta_{1.0}$ was converted to absolute viscosity according to Equation 13 in Chapter 6.



Note: See the footnote of Table 7-4 for the meaning of codes.

Figure 7-4 Viscosity at 60 °C of Residues Recovered from Marshall Samples Aged under Natural Sunlight versus Exposure Time

Table 7-5 The Aging Indices at 60 °C and Relative Severity Ranking of Residues Recovered from Marshall Samples Aged under Natural Sunlight

Age (day)	Aging Index at 60 °C and Relative Severity Ranking					
	Asphalt	BF30	MA30	MT30	CT30	BJ30A
TFOT	Aging Index	1.95	2.17	2.48	2.42	2.35
	Ranking	5	4	1	2	3
0	Aging Index	1.70	2.03	2.76	3.66	3.23
	Ranking	5	4	3	1	2
90	Aging Index	2.74	3.22	5.93	7.00	4.49
	Ranking	5	4	2	1	3
180	Aging Index	3.89	4.43	6.72	7.59	6.10
	Ranking	5	4	2	1	3
360	Aging Index	3.27	4.45	6.29	9.20	7.90
	Ranking	5	4	3	1	2
720	Aging Index	5.17	6.52	10.38	16.25	10.62
	Ranking	5	4	3	1	2
1520	Aging Index	18.74	21.10	28.78	48.40	56.56
	Ranking	5	4	3	2	1

Note:

See Table 7-4 for the meaning of codes.

The MA30 asphalt was from the same source as those MA asphalts investigated in the testing program on binders as described in Chapter 5. Thus the aging indices of the MA30 samples were compared to those obtained from the laboratory simulation methods. A similar aging index of 20 was measured from the MA asphalts aged in the 110 °C-PAV as presented in Chapter 5. For asphalts from this particular refinery source, the aging effect of 110 °C-PAV is similar to that of Marshall samples aged under natural sunlight for four years. The comparison of aging effects of 110 °C-PAV and four-year natural exposure in terms of aging index at 60 °C is shown in Figure 7-5. An aging index of 30 at 60 °C, which is approximately equal to a viscosity value of 90,000 poise at 60 °C for an AC-30, was tentatively selected as the viscosity limit for the occurrence of thermal cracking under Florida condition. This is equal to a parallel shift ($\Delta\beta$) of 1.477 in the log-log plot of viscosity versus absolute temperature. Using Equation 9 with $\beta_0 = 172.0$ and $\beta_1 = 67.1$ for a typical AC-30 in Florida [35], the temperature at which an AC-30 exhibits a viscosity of 2×10^{10} poises can be estimated as the following:

$$\mathit{log}\ (2\times10^{10}) = 1.477 + 172.0 - 67.1\times \mathit{log}\ (T)$$

$$T = 270.29\ °K = -2.71\ °C = 27.1\ °F$$

It is not unusual for pavements in Florida to reach such a temperature in the winter time.

7.5 Evaluation of Age Hardening Model

An asphalt aging model had previously been developed and used in a computerized mechanistic system for evaluation and rehabilitation of flexible pavement (REDAPS

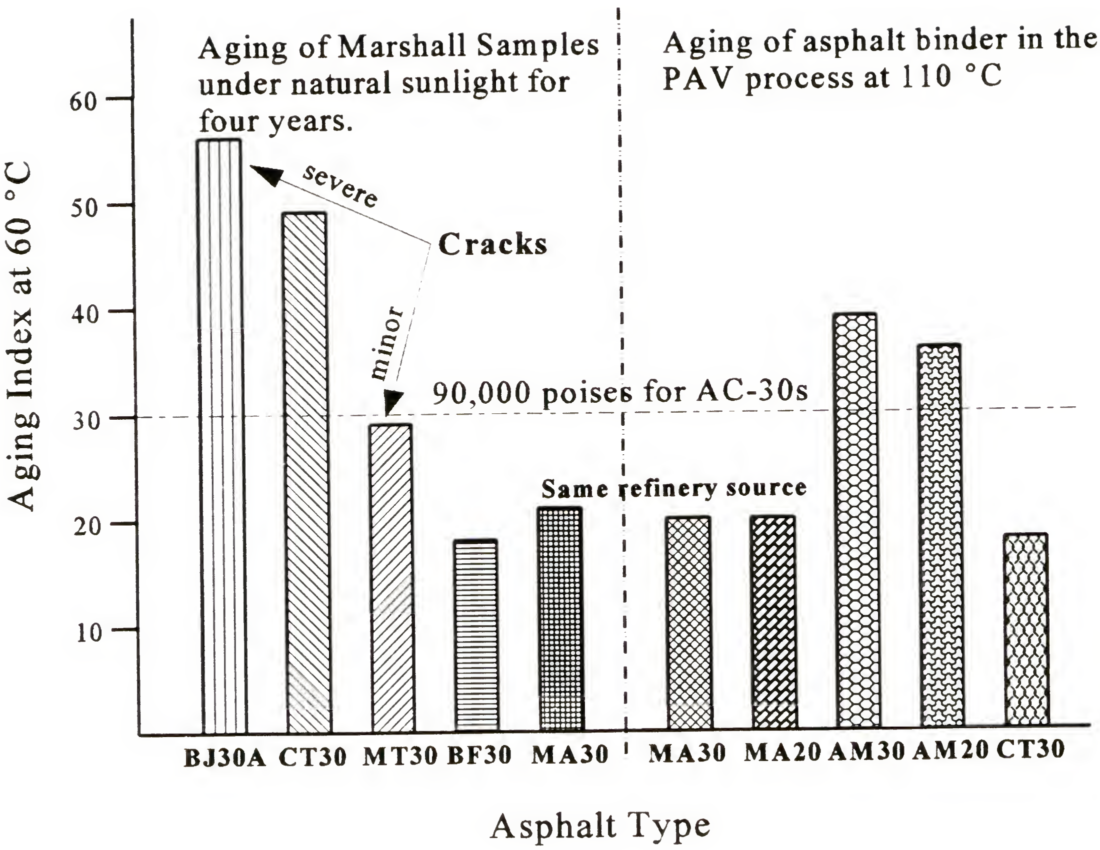


Figure 7-5 Comparison of Aging Effects of 110 °C-PAV on Binders and four-year Natural Exposure on Mixtures

Version 2). The basic assumption is that asphalt viscosity increase with age following a linear relationship on logarithmic scales. The following equation was used:

$$log\ (\eta) = A + B \times log\ (\text{days}) \tag{14}$$

The A value is equal to the logarithm of the viscosity of the binder at construction and its relationship with the original viscosity can be expressed as:

$$A = log\ (\eta_{original}) + \log\ (VR_{construction}) \tag{15}$$

The $VR_{construction}$ is the ratio of the binder viscosity at construction to its original viscosity and is usually represented by the viscosity ratio of the TFOT residue. The value of A depends on the original viscosity of the binder and the binder aging that occurs during the construction process. For an average $VR_{construction}$ of 2, the A values are 3.602 and 3.778 for a typical AC-20 and a typical AC-30, respectively. The B value is the rate of age hardening, which is a function of the aging characteristics of asphalt and the severity of environment including mainly the temperature and air void contain of the mix. A non-durable asphalt would have a higher B value.

This age hardening model was evaluated in this study by using the absolute viscosity data obtained from this study as well as those from some paving projects. These data base includes:

(1) I-75 section with one source of AC-20 monitored in the previous study [17].

(2) US-301 section I and II with the same source of AC-20 monitored in the previous study [17].

(3) Two sections with two different AC-20 asphalts in a mixing-temperature reduction study [66].

(4) Marshall samples aged in a forced-draft oven up to 90 days in a previous study [17].

(5) Marshall samples exposed to natural sunlight for fours years.

The absolute viscosity data were used to evaluate the applicability of Equation 15 and the aging hardening rates (*B*) of asphalts under Florida environment. Figure 7-6 through 7-9 show the change of absolute viscosity with pavement age in four paving projects monitored by the Material Office of FDOT. It is noticed that the relationship of viscosity and pavement age is more like an upward exponential curve than a straight line in the logarithmic scales. These relationships are consistent with those observed on the four-year-naturally-exposed Marshall samples as described in Figure 7-4.

Table 7-6 lists the summary of the results of regression analyses to relate asphalt viscosity to pavement age by using the age hardening model (Equation 14), for different paving projects and compacted samples after oven and natural aging. It is noticed that the age hardening rate (B) falls into the range of 0.1 and 0.35, which is much lower than 0.7 used in the REDAPS program. Two of the five asphalt binders (MA30 and MT30) exhibit higher B values in the natural exposure than in the forced-draft oven aging, which is beyond the expectation that asphalts age faster in the forced-draft oven. As expected, the

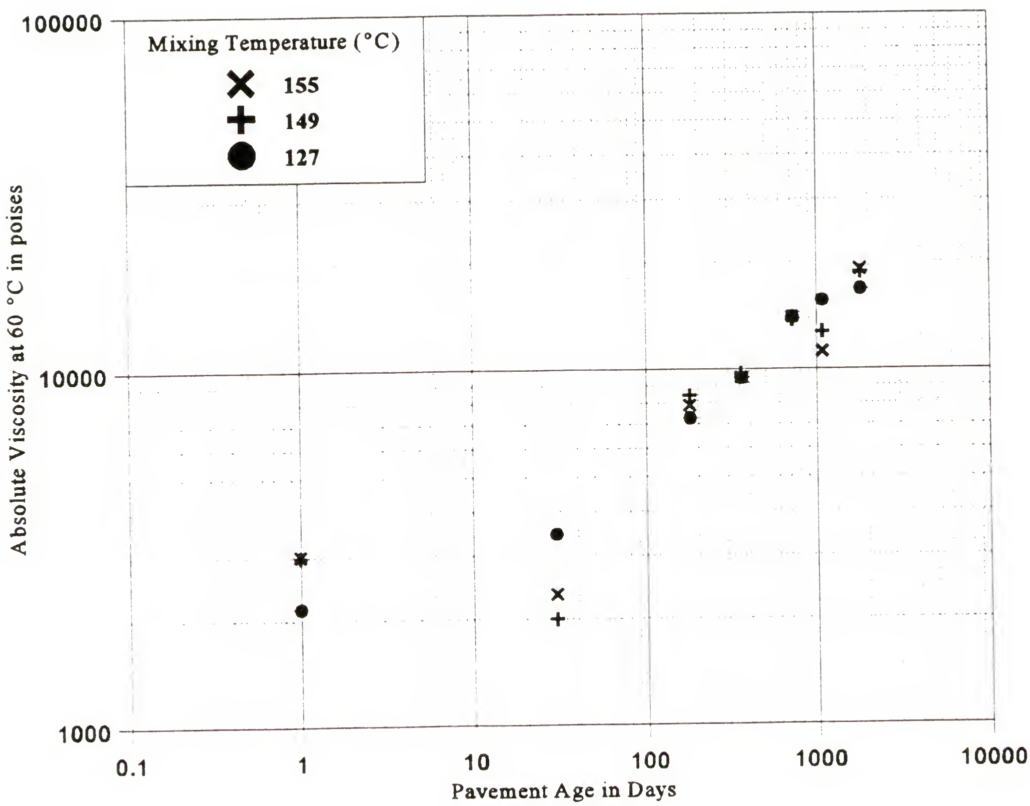


Figure 7-6 The Relationship of Absolute Viscosity and Pavement Age in FDOT Project No. 16090-3512

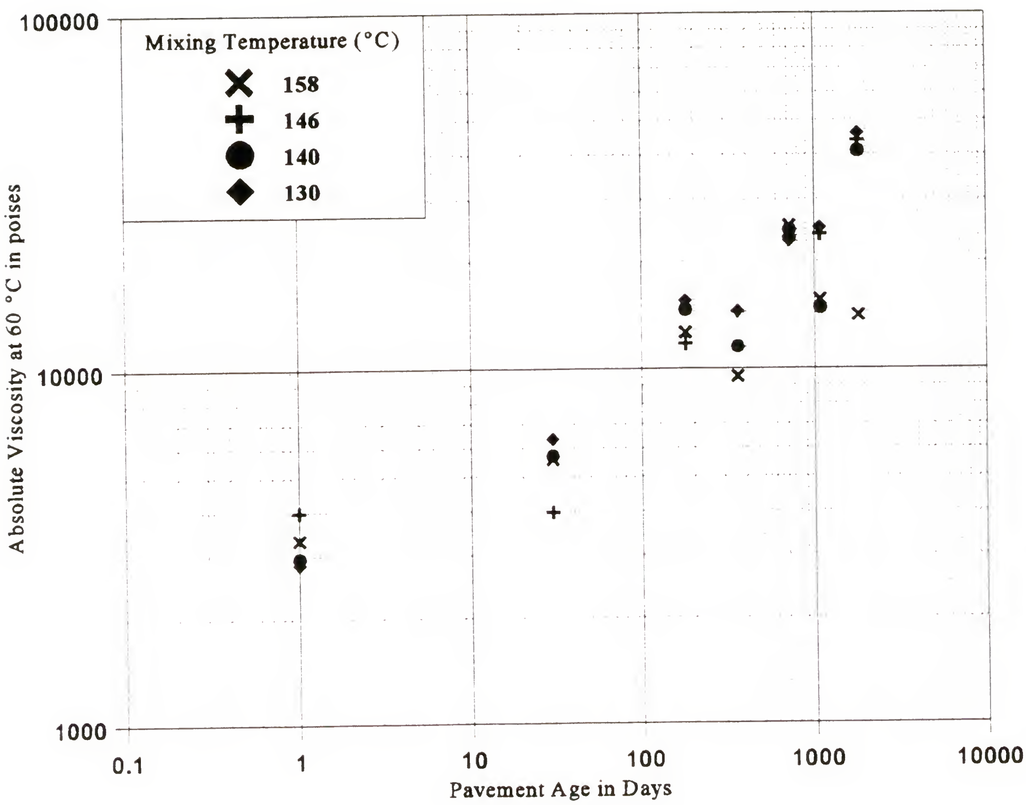


Figure 7-7 The Relationship of Absolute Viscosity and Pavement Age in FDOT Project No. 54110-3503

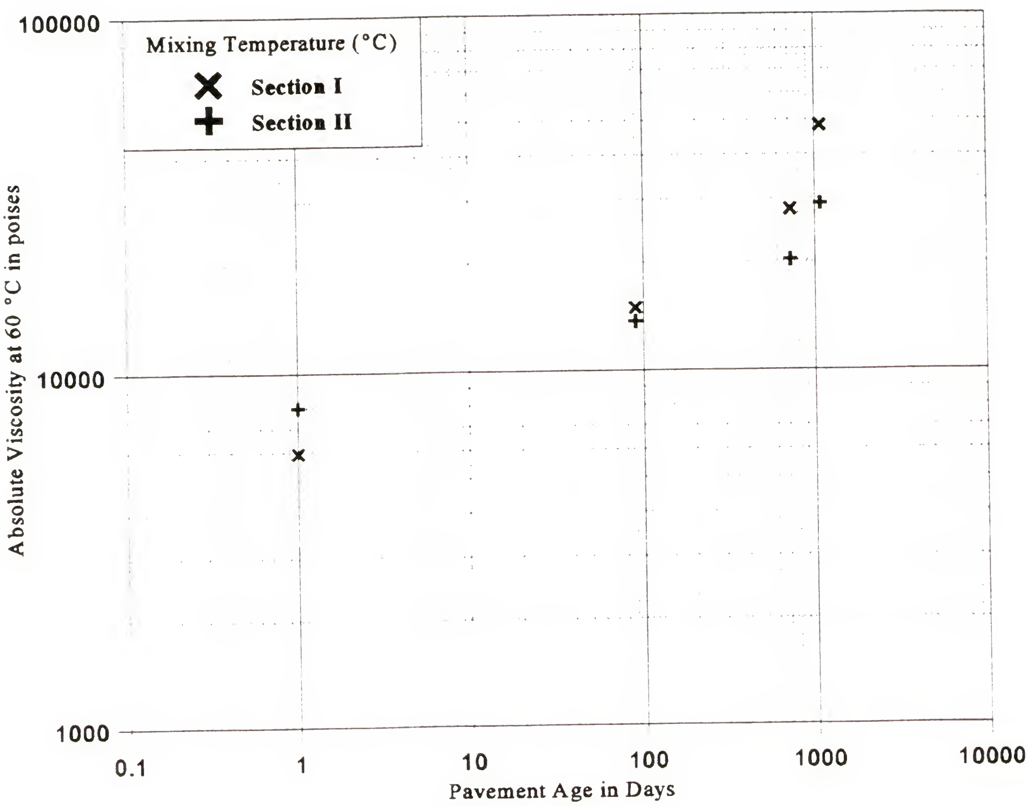


Figure 7-8 The Relationship of Absolute Viscosity and Pavement Age in FDOT Project US301 Section I and II

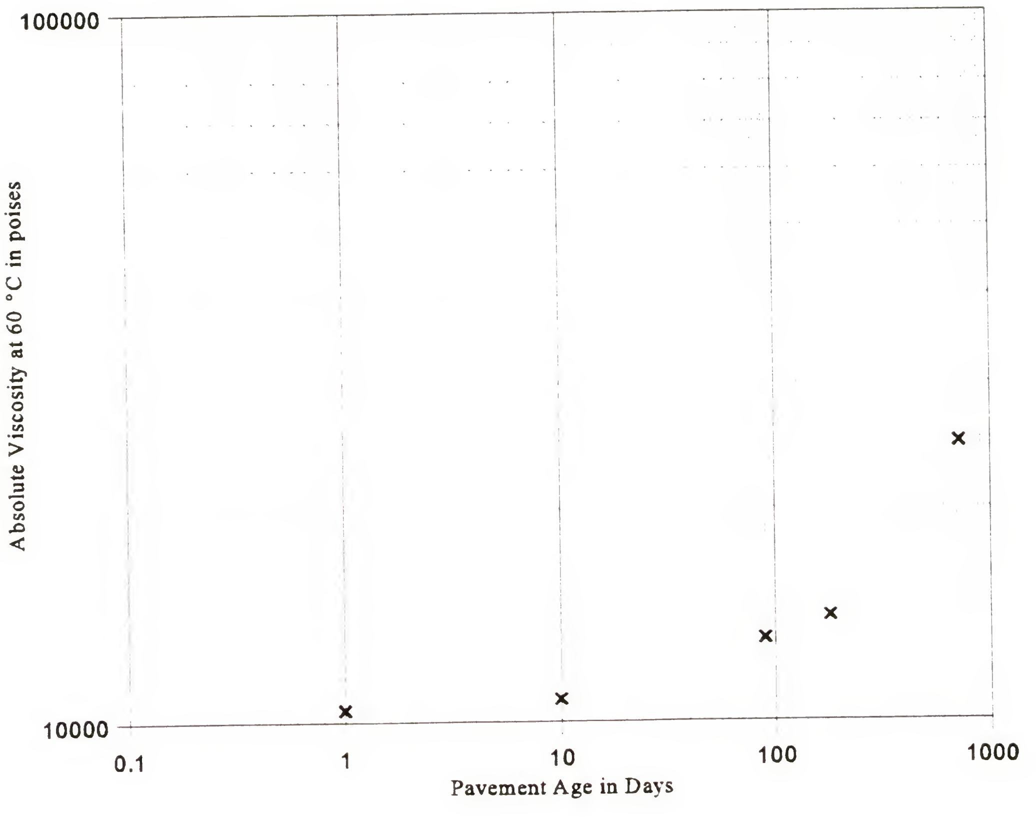


Figure 7-9 The Relationship of Absolute Viscosity and Pavement Age in FDOT Project I-75

Table 7-6 Summary of Results of Regression Analyses Using Equation 14 to Relate Asphalt Viscosity to Pavement Age for Different Projects
Regression Equation:

$$log\ (\eta) = A + B \times log\ (\text{days})$$

Project		A	B	R-Square	D. F.[1]
U.S. 301	Section I	3.7363	0.2725	0.9362	2
	Section II	3.8764	0.1663	0.9212	2
I-75		3.9579	0.1138	0.7183	3
No. 16090-3512	M.T.[2] 155	3.3076	0.2621	0.7679	5
	M.T. 149	3.2803	0.2744	0.7416	5
	M.T. 127	3.2445	0.2954	0.9472	5
No. 54110-3503	M.T. 158	3.4949	0.2348	0.8146	5
	M.T. 146	3.4131	0.3185	0.8268	5
	M.T. 140	3.4004	0.3123	0.8650	5
	M.T. 130	3.3831	0.3462	0.9489	5
Natural Exposure of Marshall Samples up to four years	BF30[3]	3.7223	0.2437	0.6045	4
	MA30	3.6877	0.2468	0.6452	4
	MT30	3.8801	0.2528	0.7165	4
	CT30	3.8869	0.2810	0.6776	4
	BJ30A	3.8470	0.2879	0.5474	4
Forced-Draft Oven at 60 °C up to 90 days	BF30	3.8211	0.2576	0.9641	2
	MA30	3.7931	0.2195	0.9416	2
	MT30	3.8957	0.2455	0.7016	2
	CT30	3.9404	0.2996	0.7368	2
	BJ30A	3.9646	0.2724	0.7677	2

Note 1: Degree of freedom.
2: Mixing temperature in °C
3: See Table 7-4 for the meaning of asphalt type.

A value is higher when higher mixing temperature is used as shown in the two temperature-reduction projects.

Table 7-7 shows the viscosities at 60 °C as predicted by the age hardening models (using the parameters in Table 7-6) along with the measured values. It can be seen that most of the predicted values are much lower than the measured ones. The predicted time for the asphalt binders to reach the viscosity value of 90,000 poises is listed in Table 7-7. The fact that BJ30A was found to have surface cracks at the age of four years strongly indicated that Equation 14 underestimate the rate of age hardening. The fact that most of the data collected in this study show a continuously increasing pattern of absolute viscosity contribute to a lower predicted value by using that age hardening model. A revised linear model comprising of a second-order term was tried. The revised model is as follows:

$$\log(\eta) = A + B \times \log(\text{days}) + C \times (\log(\text{days}))^2 \qquad (16)$$

Equation 16 represents an upward curve in the log-log plot of viscosity versus pavement age in days. The *A* value in Equation 16 is generally the same as that in Equation 14; however, both *B* and *C* are related to the age hardening rate. The value of C has more weight in influencing the viscosity, and the value of *B* could be negative. Table 7-8 lists the summary of the results of regression analyses by using the revised model (Equation 16). A higher *A* value was obtained, and half of the *B* values are negative. Table 7-9 lists the predicted viscosities along with the measured ones. The comparison of these two models can be seen in Figure 7-10 which shows the plot of the predicted

Table 7-7 Comparison of the Predicted Viscosities by Using Equation 14 with Measured Values in Different Projects

Project		Viscosity at 60 °C in poises			Years to reach 90000 poises
		Age (Days)	Predicted	Measured	
U.S. 301	Section I	1080	36552	48430	80.8
	Section II	1080	24036	29112	>>100
I-75		1080	20096	24703	>>100
No. 16090-3512	M.T.[2] 155	1800	14481	19100	>>100
	M.T. 149	1800	14912	18700	>>100
	M.T. 127	1800	16073	16800	>>100
No. 54110-3503	M.T. 158	1800	18165	14100	>>100
	M.T. 146	1800	28178	43800	>100
	M.T. 140	1800	26123	41000	>100
	M.T. 130	1800	32365	46000	94.6
Natural Exposure of Marshall Samples up to four years	BF30[3]	1440	31045	76289	>100
	MA30	1440	29321	67570	>100
	MT30	1440	47702	98132	48.6
	CT30	1440	59484	139869	17.2
	BJ30A	1440	57055	188618	19.2
Forced-Draft Oven at 60 °C up to 90 days	BF30	90	21111	18651	68.6
	MA30	90	16675	23048	>100
	MT30	90	23739	43330	56.2
	CT30	90	33565	49245	6.6
	BJ30A	90	31400	31051	11.8

Note:

See Table 7-6 for the meaning of codes.

Table 7-8 Summary of Results of Regression Analysis by Using the Revised Aging Model

Regression Equation:

$$log\ (\eta) = A + B \times log\ \text{(days)} + C \times (\ log\ \text{(days)}\ )^2$$

Project		*A*	*B*	*C*	R-Square	D. F.
U.S. 301	Section I	3.7754	0.0433	0.0775	0.9748	1
	Section II	3.9035	0.0079	0.0535	0.9700	1
I-75		4.0295	-0.1110	0.0805	0.9623	2
No. 16090-3512	M.T. 155	3.4476	-0.1239	0.1192	0.9046	4
	M.T. 149	3.4342	-0.1502	0.1311	0.8872	4
	M.T. 127	3.3204	0.0859	0.0647	0.9862	4
No. 54110-3503	M.T. 158	3.5005	0.2196	0.0047	0.8149	4
	M.T. 146	3.5845	-0.1541	0.1459	0.9762	4
	M.T. 140	3.4710	0.1176	0.0601	0.8925	4
	M.T. 130	3.4555	0.1467	0.0616	0.9747	4
Natural Exposure of Marshall Samples up to four years	BF30	3.8578	-0.2911	0.1794	0.8579	3
	MA30	3.8220	-0.2835	0.1778	0.9044	3
	MT30	3.9863	-0.1665	0.1406	0.8880	3
	CT30	4.0353	-0.3046	0.1964	0.9337	3
	BJ30A	4.0449	-0.4934	0.262	0.8982	3
Forced-Draft Oven at 60 °C up to 90 days	BF30	3.8447	0.1048	0.0831	0.9972	1
	MA30	3.8148	0.0793	0.0762	0.9792	1
	MT30	3.9701	-0.2357	0.2616	0.9652	1
	CT30	4.0268	-0.2596	0.3040	0.9877	1
	BJ30A	4.0357	-0.1874	0.2500	0.9816	1

Note

See Table 7-6 for the meaning of codes.

Table 7-9 Comparison of the Predicted Viscosities with Measured Values in Different Projects by Using the Revised Model (Equation 16)

Project		Viscosity at 60 °C in poises			Years to reach 90000 poises
		Age (Days)	Predicted	Measured	
U.S. 301	Section I	1080	41675	48430	11.7
	Section II	1080	26288	29112	62.5
I-75		1080	27135	24703	38.5
No. 16090-3512	M.T. 155	1800	20296	19100	35.5
	M.T. 149	1800	21602	18700	29.1
	M.T. 127	1800	19304	16800	69.6
No. 54110-3503	M.T. 158	1800	18415	14100	>>100
	M.T. 146	1800	42554	43800	11.9
	M.T. 140	1800	30952	41000	33.3
	M.T. 130	1800	38531	46000	21.0
Natural Exposure of Marshall Samples up to four years	BF30	1440	53452	76289	7.1
	MA30	1440	50142	67570	7.6
	MT30	1440	72938	98132	5.2
	CT30	1440	107746	139869	3.2
	BJ30A	1440	125916	188618	2.9
Forced-Draft Oven at 60 °C up to 90 days	BF30	90	23274	18651	3.3
	MA30	90	18230	23048	6.6
	MT30	90	32252	43330	0.8
	CT30	90	47915	49245	0.5
	BJ30A	90	42096	31051	0.6

Note:

See Table 7-6 for the meaning of codes.

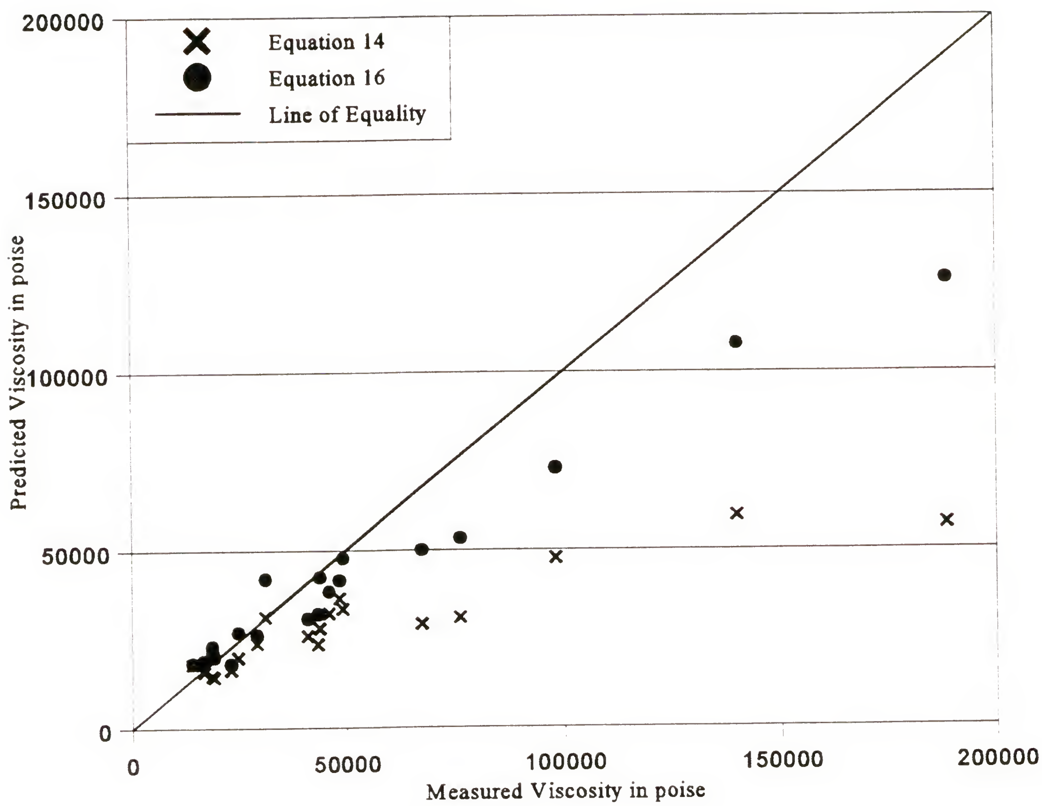


Figure 7-10 Comparison of Predicted Viscosities with the Measured Viscosities of the Two Age Hardening Models

viscosities from these two models versus the measured values. Equation 16 fits better with the data collected in this study, as shown in Figure 7-10, with a closer distance to the line of equality, particularly at the higher viscosity levels. A prediction of the time for an asphalt to reach 90,000 poises was made by using the revised model. No cracking survey report is available from all of the four paving projects. The BJ30A, which exhibited severe surface cracks on all four naturally-aged Marshall specimens at the age of four years, is predicted to reach the 90,000 poise viscosity (at 60 °C) at the age of 2.9 years under similar aging conditions. The MT30, in which one of the four Marshall samples exhibited a minor surface cracks, is predicted to reach the viscosity limit at the age of 5.2 years.

7.6 Summary of Findings

The most sensitive parameter for evaluating the aging severity of asphalts, the aging index at 60 °C, was used to evaluate the aging severities of different aging procedures on asphalt mixtures. These methods include the SHRP proposed STOA and LTOA, subjecting loose mixtures to a UV chamber and a forced-draft oven at 60 °C, and exposing Marshall samples to natural sunlight. The following conclusions were derived from these research efforts.

(1) The aging effect of the UV chamber at 60 °C on loose mixtures is consistently more severe than that of the forced-draft oven at 60 °C. Two binder aging methods, namely TFOT (TS) and high temperature TFOT (TH), aged the five asphalts in the same severity order as did the 60 °C force-draft oven on the loose mixtures for 28 days. The 100 °C-PAV aged the five asphalts in the same order as did the 60 °C UV chamber on the loose mixtures for 28 days.

(2) The PAV process at 100 °C on binders can simulate the aging effects of 60 °C UV chamber on the loose mixtures for 28 days, not only with the same relative ranking of aging potential of different asphalts, but also with similar aging severity in terms of aging index at 60 °C.

(3) The SHRP proposed STOA aged asphalts in a different severity order than did most of the methods investigated in this study and is too severe to simulate the short-term aging of asphalt binders.

(4) The SHRP proposed LTOA aged asphalts in the same severity order as the PAV processes, and produced an average aging index at 60 °C close to that produced by 100 °C-PAV on binders.

(5) The absolute viscosities at 60 °C of residues recovered from Marshall samples, which were aged under natural sunlight up to four years, kept increasing exponentially with exposure time. This is contrary to the commonly accepted theory that the rate of asphalt aging will decrease with time.

(6) Some of the compacted asphalt samples exhibited thermal cracks under natural exposure for four years. The aging severity of four-year-natural-exposure can be simulated in the laboratory by using the PAV at 110 °C.

(7) A viscosity value of 90,000 poises at 60 °C was selected, according to the results of cracked samples aged under natural sunlight for four years, to be used as the limit of the occurrence of thermal cracking in Florida condition. This is equal to an aging index of 30 for a typical AC-30, 45 for a typical AC-20, and a parallel shift ($\Delta\beta$) of 1.477 in the log-log plot of viscosity versus absolute temperature.

(8) Different asphalts showed different rates of age hardening under the same aging environment. It is difficult to find an age hardening model with fixed parameters to fit all asphalts.

CHAPTER 8
CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

A research study has been conducted to investigate different laboratory aging processes on asphalt and asphalt mixtures for development of an effective procedure to characterize asphalt durability. A few selected conventional asphalts commonly used in Florida and a few selected modified binders were subjected to different aging processes, and their aged residues were tested for comparison of aging severity. The following conclusions were derived from this study.

1. Using different recovery methods may produce recovered binders of different properties. The combination of rotavapor with reflux, which has been adopted by FDOT recently, is the most effective procedure. However, a possible increase in the viscosity of recovered binders might be noticed, as compared with those recovered by the Abson method.

2. An asphalt could age differently in different aging processes while different asphalts could age differently in the same environment. The ranking of aging severity among different asphalts could be different by using different evaluation parameters.

3. Due to the insensitivity of consistency measurements at lower temperatures, the most sensitive parameter for characterizing the aging

severity of asphalt binders was the aging index at 60 °C, which is the ratio of absolute viscosities at 60 °C of the aged residue to that of the original asphalt.

4. The Brookfield rheometer can be used to measure the viscosity of asphalt binder at 60 °C. This testing apparatus is much easier to perform than the conventional capillary tube. An equation (Equation 13 on page 145) has been established through a linear regression analysis to convert the Brookfield viscosity ($\eta_{1.0}$) to the absolute viscosity.

5. The degrees of weight loss and weight gain in the processes of high temperature TFOT are differentiable by the refinery sources. The aging index at 60 °C of a binder with a higher volatile loss could be smaller in the process of high temperature TFOT or in the process of PAV on the TFOT-aged samples. This is due to the higher possibility of skin-formation on a binder with high volatile loss and subsequent retarding of further aging. The residues aged by TFOT+PAV have lower aging indices than those aged by RTFOT+PAV.

6. Only the surface of the asphalt samples was aged by the UV light in the UV chamber. The recovered binders from the loose mixtures aged by the UV chamber showed consistently higher aging indices than those from loose mixtures aged by the forced-draft oven at the same temperature and for the same duration.

7. Low-viscosity asphalts were found to age more in the California Tilt Oven processes due to a larger contact surface caused by higher mobility in the rolling process. The CTO process for 168 hours produced the highest degree of age hardening among the four groups of aging methods. Most of the modified asphalts, except EVA modified asphalt, show less aging through higher initial viscosities in the CTO process than the control asphalt in terms of aging index at 60 °C.

8. The PAV process at 100 °C on binders can simulate the aging effects of the 60 °C UV chamber on the loose mixtures for 28 days, not only with the same relative ranking of aging potential of different asphalts but also with similar aging severity in terms of aging index at 60 °C. The aging severity of natural exposure to sunlight for four years on compacted Marshall samples can be simulated in the laboratory by using the PAV at 110 °C based on the aging index at 60 °C.

9. The conventional temperature susceptibility parameters, *PVN'* and *VTS*, were found to change after age hardening. Asphalts become less temperature susceptible after aging according to these two parameters. On the other hand, the β_1 value, which is the slope of the regression line in the log-log plot of viscosity versus absolute temperature, was essentially the same before and after aging. Due to the insensitivity of viscosity measurements and the non-Newtonian behavior of asphalts at ambient temperature, temperature susceptibility is difficult to be clearly defined.

10. In terms of the aging index at 60 °C, the effect of modifiers on reducing the aging severity of asphalts may be different when different PAV processes are used to age the binders. At 90 °C PAV, SEBS and SBR modified asphalts exhibit lower aging indices than the control asphalt. When the process temperature was increased to 100 °C, no substantial reduction of aging index was found for any of the five modified asphalts as compared with the control asphalt. The fine ground tire rubber, SEBS and SBR modified asphalts exhibit lower aging indices than the control asphalt at the process temperature of 110 °C.

11. The SHRP proposed short term oven aging (STOA) procedure (on mixtures) aged asphalts in a different severity order than did most methods (on binders) investigated in this study, and is too severe to simulate the short-term aging of asphalt binders in terms of the aging index at 60 °C. The SHRP proposed long term oven aging (LTOA) procedure (on mixtures) aged asphalts in a consistent severity order as the PAV processes (on binders) would, and produced an average aging index at 60 °C close to that by the 100 °C PAV on binders.

12. Some of the compacted Marshall samples exhibited thermal cracks after natural exposure for four years. For conventional asphalts, a viscosity limit of 90,000 poises at 60 °C was selected from the viscosity values of the cracked samples, to be used to limit the occurrence of thermal cracking of asphalt mixtures under typical Florida conditions. One of the five asphalts

used in this study showed an absolute viscosity at 60 °C higher than 90,000 poises after the process of PAV at 110 °C. This viscosity limit may not be applicable to the polymer-modified binders due to the possible difference in the mechanism of cracking.

13. The absolute viscosities at 60 °C of residues recovered from Marshall samples, which were aged under natural sunlight up to four years, kept on increasing exponentially with exposure time. Similar trends were found on the data collected from some paving projects. This is contrary to the generally accepted theory that the aging rate of asphalt would decrease with time.

8.2 Recommendations

Based on the findings of this study, the following recommendations are made:

1. The viscosity tests at 60 °C should be used to evaluate the aging severity to improve the detectability of different age hardening potential of different asphalts.
2. The PAV process at 110 °C is suggested to be used to simulate the long term aging of asphalt in service under Florida conditions. For conventional asphalts, a viscosity value of 90,000 poises at 60 °C is suggested as a limit for aged residues to reduce the possibility of thermal cracking.
3. The temperature susceptibility of an asphalt binder is important but difficult to be clearly defined. A research effort should be conducted to properly

define the temperature susceptibility and develop a simple parameter to be used in the specification of asphalt binders.

4. The UV chamber could be useful in simulating long-term aging after the development of an effective method to coat and collect thin asphalt film. Further research on the 60 °C UV chamber is suggested to develop a suitable procedure that will produce a high amount of aging.

5. The absolute viscosities of asphalt binders were found to increase exponentially with time in the field. This phenomenon should be observed and evaluated using a larger data base. Also, a study should be conducted to verify that increases in viscosity of asphalt binders occurred after several years of service and to evaluate the causes for this phenomenon.

APPENDIX A
RESULTS OF BINDER TESTS IN COMPARISON OF DIFFERENT AGING METHODS ON BINDERS

Table A-1 Results of Penetration Tests on the Five Asphalts and their Residues Aged by the 17 Aging Processes Investigated in this Study

Laboratory Aging Process	Penetration at 25 °C in 1/100 cm					
	Type	CT30	AM30	AM20	MA30	MA20
Original	1	59	63	74	57	70
	2	53	55	64	53	65
TL	1	46	43	52	47	57
	2	48	48	55	46	59
TS	1	41	43	47	41	45
	2	37	38	44	40	43
TH	1	25	32	34	31	38
	2	29	33	37	33	38
TLM	1	38	42	47	38	41
	2	41	41	47	38	45
TSM	1	27	32	37	28	33
	2	27	30	34	27	33
THM	1	17	22	22	20	25
	2	19	18	18	20	26
TF10	1	28	32	31	29	33
	2	30	32	36	31	36
TF15	1	25	27	31	27	32
	2	26	26	31	27	28
UV7	1	34	32	37	30	36
	2	30	30	30	25	34
UV14	1	34	33	38	29	35
	2	30	30	24	26	29
UV28	1	31	31	36	28	33
	2	30	32	31	28	33
C24	1	29	32	36	29	34
	2	30	33	35	29	32
C72	1	20	22	23	21	22
	2	18	22	23	21	24
C168	1	13	17	17	19	17
	2	14	18	19	17	19
P90	1	24	26	30	24	29
	2	25	26	30	25	29
P100	1	24	26	25	22	26
	2	22	23	25	23	26
P110	1	19	18	22	19	22
	2	19	19	22	19	20

Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Table A-2 Results of Infrared Spectral Analysis on the Five Asphalts and their Residues Aged by the 17 Aging Processes Investigated in this Study

Laboratory Aging Process	Carbonyl Ratio					
	Type	CT30	AM30	AM20	MA30	MA20
Original	1	0.3262	0.2922	0.2931	0.2717	0.2498
	2	0.2904	0.1998	0.2547	0.2439	0.2358
TL	1	0.3649	0.3327	0.3431	0.2793	0.2783
	2	0.3090	0.2824	0.2705	0.1834	0.1738
TS	1	0.3618	0.3282	0.3391	0.2955	0.3049
	2	0.3858	0.3247	0.2984	0.2814	0.2598
TH	1	0.4063	0.4393	0.3780	0.3330	0.3375
	2	0.3843	0.3542	0.3556	0.3111	0.3156
TLM	1	0.3717	0.3416	0.3393	0.2973	0.3187
	2	0.2868	0.2592	0.2615	0.2114	0.2243
TSM	1	0.4262	0.3966	0.4024	0.3714	0.3609
	2	0.4132	0.3718	0.3384	0.3225	0.3158
THM	1	0.5288	0.4575	0.5092	0.4418	0.4571
	2	0.5137	0.5495	0.5069	0.4566	0.3912
TF10	1	0.4435	0.3851	0.4164	0.3658	0.3906
	2	0.4701	0.3816	0.4363	0.3890	0.3890
TF15	1	0.5018	0.4554	0.4295	0.4577	0.4355
	2	0.4663	0.5019	0.4067	0.3982	0.4321
UV7	1	0.4096	0.3920	0.3912	0.3704	0.3768
	2	0.4589	0.4444	0.4919	0.4337	0.4212
UV14	1	0.4210	0.3895	0.3891	0.3630	0.3586
	2	0.4464	0.3894	0.4314	0.4095	0.3879
UV28	1	0.4173	0.3806	0.3876	0.3828	0.4028
	2	0.4322	0.4347	0.4580	0.4123	0.4716
C24	1	0.4404	0.3961	0.3996	0.3518	0.3706
	2	0.4297	0.3903	0.4117	0.3608	0.3778
C72	1	0.4821	0.3884	0.4197	0.3913	0.4274
	2	0.4789	0.3807	0.3985	0.5355	0.5835
C168	1	0.6045	0.5211	0.5501	0.5277	0.5542
	2	0.5278	0.4060	0.4931	0.4785	0.5364
P90	1	0.4640	0.4266	0.4441	0.3571	0.3764
	2	0.4365	0.3983	0.4246	0.3766	0.3774
P100	1	0.4919	0.4504	0.4728	0.4981	0.4341
	2	0.4872	0.4506	0.4663	0.3899	0.4692
P110	1	0.5761	0.5321	0.5520	0.5103	0.5170
	2	0.5756	0.5331	0.5625	0.4995	0.5276

Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Table A-3 Results of Absolute Viscosity Tests on the Five Asphalts and their Residues Aged by the 17 Aging Processes Investigated in this Study

Laboratory Aging Process	Absolute Viscosity at 60 °C in poise					
	Type	CT30	AM30	AM20	MA30	MA20
Original	1	2854	3085	2190	3038	2192
	2	2911	3207	2301	3178	2304
TL	1	4425	5106	3699	4881	3230
	2	4418	4962	3274	4239	3053
TS	1	6620	7351	5316	6088	4634
	2	5509	7558	5216	5888	5252
TH	1	13551	15656	11001	11664	8295
	2	13230	18751	11443	11204	8779
TLM	1	6538	7727	5045	7022	4923
	2	5878	7926	5580	6953	4647
TSM	1	10973	15755	10965	12413	8824
	2	12695	19159	11917	14199	9804
THM	1	82313	143754	104181	54880	34392
	2	66497	139236	72999	54716	28262
TF10	1	13456	16001	14639	14179	10983
	2	13166	15198	11839	13251	9487
TF15	1	25173	54878	24135	23287	14914
	2	21728	39535	22418	25869	16925
UV7	1	9006	13563	9878	12670	9032
	2	10339	16004	15631	21665	10261
UV14	1	9161	12497	9906	14212	9179
	2	14300	10618	22270	17031	13646
UV28	1	9430	13872	10685	15081	10193
	2	11259	13669	12827	14500	10222
C24	1	12035	12155	10025	14379	11369
	2	12352	13590	11322	15861	11090
C72	1	46920	47462	43203	43451	40910
	2	47580	44345	42826	44275	36588
C168	1	137426	122941	101821	66914	97495
	2	118085	99238	105369	98491	92689
P90	1	18182	26875	16973	25527	15509
	2	19215	27457	18528	22318	15491
P100	1	19083	27292	26687	32191	18841
	2	17558	42702	36030	29207	21336
P110	1	52144	118474	73418	61948	43507
	2	55447	131619	91315	62484	46607

Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Table A-4 Results of Schweyer Rheometer Tests at 25 °C on the Five Asphalts and their Residues Aged by the 17 Aging Processes Investigated in this Study

Laboratory Aging Process	Constant Stress (1 MPa) Viscosity at 25 °C in 10^6 poises					
	Type	CT30	AM30	AM20	MA30	MA20
Original	1	4.46	2.21	1.37	2.29	1.24
	2	2.71	1.48	2.22	2.10	1.31
TL	1	4.22	2.98	2.16	2.54	1.13
	2	4.19	3.47	2.15	2.54	1.45
TS	1	7.96	4.35	3.06	3.64	2.42
	2	6.98	3.98	2.20	3.98	1.90
TH	1	19.00	10.70	5.08	6.58	3.31
	2	16.80	10.00	5.59	5.69	3.01
TLM	1	7.34	4.25	3.44	4.87	2.17
	2	6.12	6.52	2.37	3.80	2.80
TSM	1	15.20	8.47	4.92	6.35	4.12
	2	22.40	10.10	4.21	9.41	4.09
THM	1	59.40	24.40	11.40	14.90	10.60
	2	58.00	20.60	16.10	19.70	8.89
TF10	1	15.00	9.22	5.47	5.61	2.99
	2	20.40	9.04	6.12	6.65	3.64
TF15	1	26.80	12.00	9.43	8.24	4.16
	2	22.00	15.60	6.16	8.42	4.98
UV7	1	9.70	8.84	6.78	8.23	4.74
	2	15.25	6.09	8.82	8.10	4.16
UV14	1	12.70	9.34	5.85	7.37	5.61
	2	16.40	5.88	6.97	11.80	4.66
UV28	1	18.26	9.09	5.28	10.70	4.24
	2	21.10	4.35	9.45	12.30	3.88
C24	1	14.30	7.29	5.22	8.67	5.45
	2	17.90	7.93	5.09	9.53	4.84
C72	1	57.80	21.10	21.50	22.70	12.40
	2	49.70	20.50	17.30	20.60	13.70
C168	1	198.00	60.60	57.00	43.70	42.30
	2	159.00	85.90	46.30	29.50	33.40
P90	1	21.20	13.50	8.86	11.30	4.97
	2	29.20	17.70	11.10	11.00	7.92
P100	1	25.90	16.00	11.60	18.60	6.97
	2	22.30	17.20	16.50	15.90	9.89
P110	1	71.30	38.40	20.40	20.40	12.20
	2	80.20	51.20	39.70	27.30	17.60

Note: See Table 3-1 and Table 3-2 for the meaning og codes.

Table A-5 Results of Schweyer Rheometer Tests at 5 °C on the Five Asphalts and their Residues Aged by the 17 Aging Processes Investigated in this Study

Laboratory Aging Process	Constant Stress (1MPa) Viscosity at 5 °C in 10^9 poises					
	Type	CT30	AM30	AM20	MA30	MA20
Original	1	1.52	1.05	0.35	0.62	0.35
	2	0.91	0.71	1.04	0.70	0.45
TL	1	1.73	0.99	0.63	0.85	0.83
	2	1.59	0.88	0.90	0.95	0.49
TS	1	2.64	1.46	1.16	1.56	1.00
	2	2.73	1.57	0.99	0.37	0.77
TH	1	5.89	3.31	1.84	2.18	2.20
	2	6.24	2.69	2.13	2.19	1.00
TLM	1	2.76	1.44	1.24	1.56	0.79
	2	2.37	1.83	0.90	1.40	0.78
TSM	1	6.18	3.87	2.31	2.56	1.41
	2	5.21	3.42	1.58	2.59	3.76
THM	1	13.20	6.65	5.80	5.09	3.63
	2	13.50	6.75	4.35	5.41	2.73
TF10	1	5.94	2.08	1.76	2.39	1.45
	2	5.11	2.17	1.93	2.14	0.96
TF15	1	8.09	2.81	2.65	3.26	1.22
	2	8.03	1.88	2.09	2.74	2.18
UV7	1	3.29	2.82	1.69	2.64	1.74
	2	7.81	2.76	2.82	3.87	1.76
UV14	1	4.77	3.30	1.81	4.24	1.92
	2	4.49	2.42	2.01	4.41	1.24
UV28	1	4.55	2.68	1.76	3.63	1.83
	2	5.36	3.24	1.67	3.92	1.90
C24	1	5.05	4.04	2.30	2.64	1.99
	2	8.07	3.78	1.90	4.08	1.64
C72	1	30.20	8.36	7.10	8.04	2.82
	2	18.50	8.30	5.18	9.11	3.83
C168	1	41.60	30.90	27.10	8.55	6.88
	2	44.80	26.60	36.40	14.44	21.70
P90	1	9.77	6.82	2.11	2.86	1.41
	2	16.30	10.70	5.75	4.36	1.28
P100	1	12.43	4.56	3.14	9.31	1.94
	2	14.24	8.93	7.52	5.16	2.40
P110	1	28.10	23.90	15.00	7.46	4.72
	2	23.30	29.90	9.35	7.91	2.73

Note: See Table 3-1 and Table 3-2 for the meaning of codes.

APPENDIX B
RESULTS OF BINDER TESTS IN THE AGING CHARACTERISTICS OF MODIFIED BINDERS

Table B-1 Results of Penetration Tests on the Modified Binders and their Residues Aged by the CTO and the PAV Processes

Laboratory Aging Process	Penetration at 25 °C in 1/100 cm						
	Type	CT30	GTR	CB	SEBS	EVA	SBR
Original	1	59	46	50	26	44	50
	2	53	46	46	23	35	48
	Mean	56	46	48	24	40	49
C24	1	29	28	28	21	23	-
	2	30	27	26	20	22	-
C72	1	20	20	18	17	17	-
	2	18	19	18	16	17	-
C168	1	13	17	14	14	12	-
	2	14	16	14	14	11	-
P90	1	24	25	22	25	46	39
	2	25	23	22	24	43	43
P100	1	24	22	12	22	21	41
	2	22	21	20	20	22	43
P110	1	19	17	16	17	29	36
	2	19	18	15	18	20	37
Penetration Retained Percent (%)							
C24	1	49	61	56	81	52	-
	2	57	59	57	87	63	-
C72	1	34	43	36	65	39	-
	2	34	41	39	70	49	-
C168	1	22	37	28	54	27	-
	2	26	35	30	61	31	-
P90	1	43	54	46	100	100	80
	2	45	50	46	100	100	88
P100	1	43	48	25	92	52	84
	2	39	46	42	83	55	88
P110	1	34	37	33	71	72	73
	2	34	39	31	75	50	76

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.

Table B-2 Results of Infrared Spectral Analysis on the Modified Binders and their Residues Aged by the CTO and the PAV Processes

Laboratory Aging Process	Carbonyl Ratio						
	Type	CT30	GTR	CB	SEBS	EVA	SBR
Original	1	0.3262	0.3279	-	0.3087	0.4017	0.2387
	2	0.2904	0.3149	-	0.3000	0.3732	0.2031
	Mean	0.3083	0.3214	-	0.3044	0.3874	0.2209
C24	1	0.4404	0.4203	-	0.3556	0.5222	-
	2	0.4297	0.4167	-	0.2474	0.3746	-
C72	1	0.4821	0.5306	-	0.4161	0.6362	-
	2	0.4789	0.5455	-	0.3593	0.5573	-
C168	1	0.6045	0.5714	-	0.4515	0.7214	-
	2	0.5278	0.5637	-	0.4339	0.7019	-
P90	1	0.4640	0.4363	-	0.3993	0.5644	0.3868
	2	0.4365	0.4499	-	0.4247	0.5240	0.3813
P100	1	0.4919	0.4444	-	0.4385	0.5100	0.4722
	2	0.4872	0.4721	-	0.4323	0.5359	0.4634
P110	1	0.5761	0.5572	-	0.4845	0.5856	0.5395
	2	0.5756	0.5302	-	0.5070	0.5801	0.4862
Carbonyl Ratio Index							
C24	1	1.35	1.28	-	1.15	1.30	1.28
	2	1.48	1.32	-	0.82	1.00	1.75
C72	1	1.48	1.62	-	1.35	1.58	1.46
	2	1.65	1.73	-	1.20	1.49	2.39
C168	1	1.85	1.74	-	1.46	1.80	1.77
	2	1.82	1.79	-	1.45	1.88	2.74
P90	1	1.50	1.36	-	1.31	1.46	1.75
	2	1.42	1.40	-	1.40	1.35	1.73
P100	1	1.60	1.38	-	1.44	1.32	2.14
	2	1.58	1.47	-	1.42	1.38	2.10
P110	1	1.87	1.73	-	1.59	1.51	2.44
	2	1.87	1.65	-	1.66	1.50	2.20

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.
The infrared spectral analysis is not applicable on the carbon black modified binders beacuse of the occurrence of too many peaks in the spectrum.

Table B-3 Results of Absolute Viscosity Tests on the Modified Binders and their Residues Aged by the CTO and the PAV Processes

Laboratory Aging Process	Absolute Viscosity at 60 °C in Poise						
	Type	CT30	GTR	CB	SEBS	EVA	SBR
Original	1	2854	6024	3854	19357	4122	8722
	2	2911	5820	5345	30532	5639	6086
	Mean	2883	5922	4600	24944	4880	7404
C24	1	12035	24322	13190	66976	18037	-
	2	12352	23221	13833	50593	23477	-
C72	1	46920	57498	35774	95594	87389	-
	2	47580	50403	37395	71957	98061	-
C168	1	137426	123543	96825	140976	1275428	-
	2	118085	120938	98532	150374	2543276	-
P90	1	18182	34947	27117	93360	37639	26539
	2	19215	34005	27963	108540	39145	26282
P100	1	19083	44571	42246	135341	50388	36792
	2	17558	45837	39408	143172	67609	40930
P110	1	52144	98506	97739	301740	210709	53405
	2	55447	78269	76982	255201	179999	60221
Aging Index at 60 °C							
C24	1	4.22	3.99	2.59	3.46	4.38	-
	2	4.24	4.04	3.42	1.66	4.16	-
C72	1	16.34	8.66	7.00	4.94	21.20	-
	2	16.44	9.54	9.28	2.36	17.39	-
C168	1	40.57	20.78	18.43	7.28	451.02	-
	2	48.15	20.51	24.12	4.93	309.42	-
P90	1	6.31	5.90	5.90	3.74	7.71	3.58
	2	6.66	5.74	6.08	4.35	8.02	3.55
P100	1	6.62	7.53	9.18	5.43	10.33	4.97
	2	6.09	7.74	8.57	5.74	13.85	5.53
P110	1	18.09	16.63	21.25	12.10	43.18	7.21
	2	19.23	13.22	16.74	10.23	36.89	8.13

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.

Table B-4 Results of Schweyer Rheometer Tests at 25 °C on the Modified Binders and their Residues Aged by the CTO and the PAV Processes

Laboratory Aging Process	Constant Strress (1 MPa) Viscosity at 25 °C in 10^6 Poises						
	Type	CT30	GTR	CB	SEBS	EVA	SBR
Original	1	4.46	2.73	1.69	28.30	7.13	0.52
	2	2.71	4.31	3.09	16.00	5.63	1.52
	Mean	3.58	3.52	2.39	22.15	6.38	1.02
C24	1	14.30	32.20	18.60	40.10	8.10	-
	2	17.90	24.70	16.70	49.30	12.20	-
C72	1	57.80	55.80	36.20	93.90	18.00	-
	2	49.70	21.50	54.00	74.30	30.30	-
C168	1	198.00	114.00	87.00	154.00	28.00	-
	2	159.00	70.70	92.10	154.00	113.00	-
P90	1	21.20	34.20	26.30	115.00	23.00	33.60
	2	29.20	35.90	35.10	131.00	25.10	2.56
P100	1	25.90	34.80	43.40	160.00	19.80	33.0
	2	22.30	45.50	55.80	148.00	31.20	6.32
P110	1	71.30	84.80	78.70	207.00	72.40	10.60
	2	80.20	70.80	90.40	189.00	69.50	11.30
Aging Index at 25°C							
C24	1	3.20	11.79	11.01	1.42	1.14	-
	2	6.63	5.73	5.40	3.08	2.17	-
C72	1	12.94	20.44	21.42	3.32	2.52	-
	2	18.38	4.99	17.48	4.64	5.38	-
C168	1	44.37	41.76	51.48	5.44	3.93	-
	2	58.58	16.40	29.81	9.63	20.07	-
P90	1	5.92	9.72	11.00	5.19	3.60	32.94
	2	8.16	10.20	14.69	5.91	3.93	2.51
P100	1	7.23	9.89	18.19	7.22	3.10	32.35
	2	6.23	12.93	23.35	6.68	4.89	6.20
P110	1	19.92	24.09	32.93	9.34	11.35	10.39
	2	22.40	20.11	37.82	8.53	10.89	11.07

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.

Table B-5 Results of Schweyer Rheometer Tests at 5 °C on the Modified Binders and their Residues Aged by the CTO and the PAV Processes

Laboratory Aging Process	Constant Stress (1 MPa) Viscosity at 5 °C in 10^9 Poises						
	Type	CT30	GTR	CB	SEBS	EVA	SBR
Original	1	1.52	1.00	0.65	3.69	4.51	0.87
	2	0.91	0.99	1.08	6.95	6.60	5.37
	Mean	1.22	1.00	0.87	5.30	5.56	3.12
C24	1	5.05	6.23	4.28	6.21	3.33	-
	2	8.07	6.86	4.09	4.19	8.37	-
C72	1	30.20	11.80	15.80	12.40	4.33	-
	2	18.50	6.78	15.50	13.60	9.90	-
C168	1	41.60	12.30	42.30	95.70	55.50	-
	2	44.80	17.80	36.60	47.20	24.00	-
P90	1	9.77	7.73	11.40	17.92	10.63	3.80
	2	16.30	9.76	12.20	20.61	13.74	1.23
P100	1	12.43	12.50	12.70	28.63	11.17	5.48
	2	14.24	19.90	23.00	27.14	20.11	10.22
P110	1	28.10	22.90	42.30	30.51	19.22	11.26
	2	23.30	13.30	32.60	38.91	23.20	24.53
Aging Index at 5 °C							
C24	1	3.32	6.23	6.56	1.68	0.74	-
	2	8.84	6.93	3.79	0.61	1.27	-
C72	1	19.80	11.80	24.23	3.36	0.96	-
	2	20.26	6.85	14.35	1.97	1.50	-
C168	1	27.33	12.30	64.88	25.93	12.31	-
	2	49.01	17.98	33.89	6.82	3.64	-
P90	1	8.01	7.73	13.10	3.38	1.91	1.22
	2	13.36	9.76	14.02	3.89	2.47	0.39
P100	1	10.19	12.50	14.60	5.40	2.01	1.76
	2	11.67	19.90	26.44	5.12	3.62	3.28
P110	1	23.03	22.90	48.62	5.76	3.46	3.61
	2	19.10	13.30	37.47	7.34	4.17	7.86

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.

APPENDIX C
BROOKFIELD RHEOMETER TEST DATA AND THEIR CORRESPONDING ABSOLUTE VISCOSITY

Table C The Brookfield Viscosity Data and their Corresponding Absolute Viscosity

Asphalt Type	**Aging Process**	**Absolute Viscosity in Poise**	**Brookfield Viscosity, $\eta_{1.0}$ in Poise**
CT30	Original	2883	3198
AM30	Original	3146	3563
AM20	Original	2246	2534
MA30	Original	3108	3655
MA20	Original	2248	2476
GTR	Original	5922	5703
CB	Original	4600	4232
SEBS	Original	24944	23500
EVA	Original	4880	5745
SBR	Original	7404	7616
CT30	C24	12035	13676
GTR	C24	24322	21744
CB	C24	13190	13131
SEBS	C24	50593	44342
EVA	C24	23477	23407
CT30	C72	46920	44458
GTR	C72	57498	33504
CB	C72	35774	37406
SEBS	C72	71957	70797
EVA	C72	98061	76832
CT30	C168	118085	104969
GTR	C168	123543	73447
CB	C168	96825	76906
SEBS	C168	150347	137600
EVA	C168	2543276	380238
CT30	P90	18182	16115
CT30	P90	19215	17725
AM30	P90	26875	22211
AM30	P90	27457	23990
AM20	P90	16973	17408
AM20	P90	18528	16516
MA30	P90	25527	22605
MA30	P90	22318	20950
MA20	P90	15509	15372
MA20	P90	15491	16409

Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Table C Continued

Asphalt Type	Aging Process	Absolute Viscosity in Poise	Brookfield Viscosity, $\eta_{1.0}$ in Poise
GTR	P90	34947	28392
GTR	P90	34005	27781
CB	P90	27117	23162
CB	P90	27963	19417
SEBS	P90	93360	110793
SEBS	P90	108540	119403
EVA	P90	37639	29795
EVA	P90	39154	34216
SBR	P90	26539	29300
SBR	P90	26282	22583
CT30	P100	19083	19361
CT30	P100	17585	23010
AM30	P100	27292	26320
AM30	P100	42720	34711
AM20	P100	26687	20600
AM20	P100	36030	25689
MA30	P100	32191	29745
MA30	P100	29207	27425
MA20	P100	18841	17800
MA20	P100	21363	17721
GTR	P100	44571	35546
GTR	P100	45837	39084
CB	P100	42246	30157
CB	P100	39408	36582
SEBS	P100	135341	203133
SEBS	P100	143172	188524
EVA	P100	50388	41249
EVA	P100	67609	46095
SBR	P100	36792	30400
SBR	P100	40930	38000
CT30	P110	52144	44246
CT30	P110	55447	45714
AM30	P110	118474	66051
AM30	P110	131619	79014
AM20	P110	73418	45914
AM20	P110	9115	63730

Note: See Table 3-1 and Table 3-2 for the meaning of codes.

Table C Continued

Asphalt Type	**Aging Process**	**Absolute Viscosity in Poise**	**Brookfield Viscosity, $\eta_{1.0}$ in Poise**
MA30	P110	61948	54136
MA30	P110	62484	53820
MA20	P110	43507	39164
MA20	P110	46607	42140
GTR	P110	98506	65975
GTR	P110	78269	60331
CB	P110	97739	54931
CB	P110	76982	62838
SEBS	P110	301740	235306
SEBS	P110	255201	121412
EVA	P110	210709	154049
EVA	P110	179999	198342
SBR	P110	53405	51400
SBR	P110	60221	43700

APPENDIX D
TEST RESULTS IN THE COMPARISON OF TFOT AND RTFOT IN THE PROCESS OF PRESSURE AGING VESSEL

Table D Brookfield Viscosity at 1 sec^{-1}, 60 °C (in poise) of the Residues of Different PAV Process

Asphalt	CT30	AM30	AM20	MA30	MA20	GTR	CB	SBR
Original	3198	3563	2534	3655	2476	5703	4232	7616
RTFOT	8216	12030	8215	11547	7832	17049	14299	-
TFOT	6453	11395	7762	8473	6098	11246	9672	22000
RTFOT+PAV at 90°C	20527	33664	25262	29791	21747	38650	29515	-
	19748	31936	22236	27659	19304	37923	33759	-
RTFOT+PAV at 100°C	30033	40843	35689	41534	29325	54433	50244	-
	33043	51095	36795	42258	32434	52372	49264	
RTFOT+PAV at 110°C	59401	137997	84113	82750	53595	127803	91295	-
	73718	144810	95836	69221	56000	101030	71865	-
TFOT+PAV at 90°C	19422	27948	20235	25786	18280	30751	26981	38500
	18085	28023	20270	23642	17429	29348	27763	33900
TFOT+PAV at 100°C	29737	45239	33859	41000	30014	46746	46175	41100
	28645	48943	33397	40955	29119	42538	45057	48500
TFOT+PAV at 110°C	56537	96477	63530	77288	45199	77284	93882	43500
	56271	121750	74902	69712	42924	71755	74781	60600

Note:

See Table 3-1 and Table 3-2 for the meaning of codes.

REFERENCES

1. Tia, M., B.E. Ruth, "Improved Asphalt Cement Specifications to Ensure Better Performance," Research Proposal, WPI 0510514, Department of Civil Engineering, University of Florida, Gainesville, October 1990.

2. Finn, F.N., M.T. Yapp, J.S. Coplantz, and A.Z. Durrani, "Asphalt Properties and Relationship to Pavement Performance: Literature Review", SR-ARE-4-003A-89-3, Strategic Highway Research Program, National Research Council, Washington, D.C., 1990.

3. Monismith, C.L., R.G. Hicks, and F.N. Finn, "Evaluation of Tests for Asphalt-Aggregate Mixtures Which Related to Field Performance," Proceedings of the Fourth International RILEM Symposium, Budapest, Hungary, 1990, pp. 504-539.

4. "Relationship of Asphalt Cement Properties of Pavement Durability," NCHRP Synthesis of Highway Practice 59, TRB, National Research Council, Washington, D.C., 1979.

5. McLeod, N.W., "Relationship of Paving Temperature Susceptibility as Measured by PVN by Paving Asphalt Specifications, Asphalt Paving Mixture Design and Asphalt Pavement Performance," Association of Asphalt Paving Technologists Vol. 58, 1989, pp.410-489.

6. "Low-Temperature Properties of Paving Asphalt Cements," State of the Art Report 7, Committee on Characteristics of Bituminous Materials, TRB, National Research Council, Washington, D.C., 1988.

7. Schmidt, R.J., "Use of ASTM Tests to Predict Low-Temperature Stiffness of Asphalt Mixes," TRR 544, TRB, National Research Council, Washington, D.C., 1975, pp.33-45.

8. Anderson, D.A., Christensen, D.W., and Bahia, H., "Physical Properties of Asphalt Cement and the Development of Performance-Related Specification," Association of Asphalt Paving Technologists Vol. 60, 1991, pp.437-474.

9. W. H. Goetz and L. E. Wood, "Bituminous Materials and Mixtures," Highway Engineering Handbook, Section 18, McGraw-Hill, N.Y., 1960.

10. Goodrich, J.L., J.E. Goodrich, and W.J. Kari, "Asphalt Composition Tests: Their Application and Relation to Field Performance," TRR No. 1096, National Research Council, Washington, D.C., 1986, pp. 146-167.

11. Corbett, L.C., "Relationship Between Composition and Physical Properties of Asphalt," Association of Asphalt Paving Technologists Vol. 39, 1970, pp.481-491.

12. Welborn, J.Y., E.R. Oglio, and J.A. Zenewitz, " A Study of Viscosity-Graded Asphalt Cements," Association of Asphalt Paving Technologists Vol. 38, 1969, pp.19-60.

13. Corbett, L.W. and R.E. Merz, "Asphalt Binder Hardening in the Michigan Test Road After 18 Years of Service," TRR No. 544, National Research Council, Washington, D.C., 1975, pp.27-34.

14. Petersen, J.C., "Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art," TRR No. 999, National Research Council, Washington, D.C., 1984, pp.13-30.

15. Burr, B.L., R.R. Davison, H.B. Jemison, C.T. Glover, and J.A. Bullin, "Asphalt Hardening in Extraction solvents," a paper prepared for presentation at the 70th Annual Meeting of the Transportation Research Board, Washington, D.C., January, 1991.

16. Cipione, C.A., R.R. Davison, B.L. Burr, C.J. Glover, and J.A. Bullin, "Evaluation of Solvents for the Extraction of Residual Asphalt from Aggregates," a paper prepared for presentation at the 70th Annual Meeting of the Transportation Research Board, Washington, D.C., January, 1991.

17. Tia, M., B.E. Ruth, J. Shiau, S. Huang, and D. Richardson, "Evaluation of Criteria for Improved Durability of Asphalt," Final Report, UF Project No. 4910450425412, Department of Civil Engineering, University of Florida, Gainesville, December, 1990.

18. H. L. Von Quintus, J. A. Scherocman, C. S. Hughes and Y. W. Kennedy, "Asphalt-Aggregate Mixture Analysis System - AAMAS", National Cooperative Highway Research Program, Report No. 338, TRB, Washington, D.C., March 1991. pp. 131.

19. Ruth, B.E., L.A.K. Bloy, and A.A. Avital, "Prediction of Pavement Cracking at Low Temperatures," Association of Asphalt Paving Technologists, Vol. 51, 1982, pp.53-103.

20. Tia, M., B.E. Ruth, C.T. Chari, J. Shiau, D. Richardson, and J. Williams, "Investigation of Original and In-service Asphalt Properties for the Development of Improved Specifications-Final Phase of Testing and Analysis," Final Report, UF Project No. 4910450420812, Department of Civil Engineering, University of Florida, Gainesville, July, 1988.

21. Bell, C.A., Y. AbWahab, M.E. Cristi, "Investigation of Laboratory Aging Procedures for Asphalt-Aggregate Mixtures," a paper prepared for presentation at the 70th Annual Meeting of the Transportation Research Board, Washington, D.C., January, 1991.

22. "Standard Method of Indirect Tension Test for Resilient Modulus of Bituminous Mixtures" ASTM D4123-82, Annual Book of ASTM Standards Vol. 04.03, 1990.

23. Kim, O.K., C.A. Bell, J.E. Wilson, and G. Boyle, "Development of Laboratory Oxidative Aging Procedures for Asphalt Cements and Asphalt Mixtures," TRR No. 1115, Washington, D.C., 1987, pp. 101-112.

24. "Development and Validation of Performance Prediction Models and Specifications for Asphalt Binders and Paving Mixes," SHRP-A-357, Contract A-005, Product No. 1012, October 1993.

25. Tia, Mang, Ruth, B. E., Josephson, L. I., and Chari, C., "Preliminary Investigation of Original and In-Service Asphalt Properties for the Development of Improved Specifications," Final Report, Project 245-D53, State Project No. 99700-7361, 1986, Department of Civil Engineering , University of Florida, Gainesville.

26. Chari, C.T., Ruth, B.E., Tia, M., and Page, G.C., "Evaluation of Age Hardening on Asphalts and Mixtures," Association of Asphalt Paving Technologists Vol. 59, 1990, pp. 176 - 239.

27. Petersen, J.C., "Quantitative Functional Group Analysis of Asphalts Using Differential Infrared Spectrometry and Selective Chemical Reactions- Theory and Application," TRR No. 1096, Washington, D.C., 1986, pp.1-11.

28. "Specification for Penetration-Graded Asphalt Cement for Use in Pavement Construction," ASTM D946-82, Annual Book of ASTM Standards, Vol. 04.03, 1990.

29. "Specification for Viscosity-Graded-Asphalt Cement for Use in Pavement Construction," ASTM D3381-83, Annual Book of ASTM Standards, Vol. 04.03, 1990.

30. Jastrzebski, Z.D., The Nature and Properties of Engineering Materials, third edition, 1987, chapter 7, PWS-KENT Publishing Company.

31. Kandhal, P.S., L.D. Sandvig, and M.E. Wenger, "Shear Susceptibility of Asphalt in Relation to Pavement Performance," Association of Asphalt Paving Technologists Vol. 42, 1973, pp.99-125.

32. Tia, M., and B.E. Ruth, "Basic Rheology and Rheological Concepts Established by H.E. Schweyer," Asphalt Rheology: Relationships to Mixtures, ASTM STP 941, 1987, pp.118-145.

33. Roberts, F.L., P.S. Kandhal, E.R. Brown, D.Y. Lee, and T.W. Kennedy, Hot Mix Asphalt Materials, Mixture Design and Construction, NAPA Education Foundation, Lanham, Maryland, 1991.

34. Garrick, N.W., "Empirical Equations for Determining the Effects of Temperature and Shear Rate on the Viscosity of Asphalt Cements," Association of Asphalt Paving Technologists Vol. 61, 1992, pp.11.

35. Guan, L., B. E. Ruth, and R. Roque, "A Computerized Mechanistic System for Evaluation and Rehabilitation of Flexible Pavements," Association of Asphalt Paving Technologists Vol. 60, 1991, pp. 373.

36. Page, G.C., K.H. Murphy, B.E. Ruth, and R. Roque, "Asphalt Binder Hardening," Association of Asphalt Paving Technologists, Vol. 54, 1985, pp.140-167.

37. Ruth, B.E., Tia, M., and Guan, L., "Structural Characterization and Stress Analysis of Flexible Pavement System: Rehabiliation Design," Final Report to FDOT, State Project No. 99700-7351-010, WPI No. 0510318, Department of Civil Engineering, University of Florida, Gainesville, January, 1990.

38. "Standard Test Methods for Quantitative Extraction of Bitumen from Bituminous Paving Mixtures," ASTM D2172-81, Annual Book of ASTM Standards, Vol. 04.03, 1990.

39. "Standard Test Method for Recovery of Asphalt from Solution by Abson Method," ASTM D1856-79, Annual Book of ASTM Standards, Vol. 04.03, 1990.

40. AASHTO Materials Reference Laboratory Report for Bituminous Concrete Proficiency Samples, Reports from 1987, 1988, 1989 Tests, AASHTO Materials Reference Laboratory at the National Bureau of Standards, Gaithersburg, Md.

41. M. Stroup-Gardiner, D. E. Newcomb, and J. A. Epps, "Precision of Methods for Determining Asphalt Cement Content," Transportation Research Record, 1228, TRB, National Research Council, Washington, D.C., 1989, pp.156-167.

42. Burr, B.L., Davison, H.B., Glover, C.J., and Bullin, J.A., "New Apparatus and Procedure for the Extraction and Recovery of Asphalt Binder from Pavement Mixtures," Transportation Research Record, No. 1391, TRB, National Research Council, Washington, D.C., 1993.

43. "Standard Test Method for Recovery of Asphalt from Solution Using the Rotavapor Apparatus," Draft 7, March 21, ASTM Committee Meeting, 1991.

44. "Method of Recovering Asphalt Cement from Solvent and Asphalt Solution," Georgia Department of Transportation, GDT-119, Atlanta, 1990.

45. Welborn, J.Y., "Physical Properties as Related to Asphalt Durability: State of the Art," TRR No. 999, Washington, D.C., 1984, pp31-36.

46. "Standard Test Method for Effect of Heat and Air on Asphaltic Materials (Thin-Film Oven Test)," ASTM D1754-83, Annual Books of ASTM Standards, Vol. 04.03, 1990.

47. "Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test)," ASTM D2872-80, Annual Books of ASTM Standards, Vol. 04.03, 1990.

48. Schmidt, R.J., "Laboratory Measurement of the Durability of Paving Asphalts," Viscosity Testing of Asphalt and Experience with Viscosity Graded Specifications, ASTM STP 532, 1972, pp.79-99.

49. Schmidt, R.J. and Santucci, L.E., "The Effect of Asphalt Properties on the Fatigue Cracking of Asphalt Concrete on the Zaca-Wigmore Test Project", Association of Asphalt Paving Technologists Vol. 38, 1969. p.39.

50. Kemp, G.R. and Predoehl, N.H., "An Investigation of the Effectiveness of Asphalt Durability Tests," Final Report, FHWA/CA/TL-80/14, 1980.

51. Petersen, J.D., "Effect of Physical and Physicochemical Factors on Asphalt Oxidative Aging," Proceedings, First Materials Engineering Congress, American Society of Civil Engineers, Denver, August 1990, pp.244-253.

52. Button, J.W., Jawle, M., Jagadam, V., and Little, D., "Evaluation and Development of a Pressure Aging Vessel for Asphalt Cement," Transportation Research Record, No. 1391, TRB, National Research Council, Washington, D.C., 1993.

53. Lee, D.Y., "Development of a Laboratory Durability Test for Asphalts," Highway Research Record 231, HRB, National Research Council, Washington, D.C., 1968, pp.34-49.

54. "SHRP Asphalt Binder Test Methods - A Illustrated Overview," National Asphalt Training Center, Demonstration Project 101, September 1993, Asphalt Institute, Research Center, Lexington, KY.

55. Beaton, J.L. and Sherman, G.B., Minutes of 9th Pacific Coast Users and Producers Conference, 1971.

56. "Method for Determining Asphalt Durability Using the California Tilt-Oven Durability Test," California Test 374, November 1, 1983.

57. "Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)," AASHTO Designation: PP1, Edition 1A, August 1993, American Association of State Highway and Transportation Officials, Washington, D.C.

58. Bell, C.A., Sosnovske, D., and Kliewer, J.E., "Relating Asphalt and Aggregate Properties and their Laboratory Aging to Field Performance of Asphalt Mixtures," A paper presented at the 73rd Annual Meeting of Transportation Research Board, January 10-14, 1994, Washington, D.C.

59. "IEC Operation Manual OM7165," Revision 3, International Equipment Company, Needham Heights, MA, pp. 29.

60. "More Solution to Sticky Problems - A Guide to Getting More from your Brookfield Viscometer," Brookfield Engineering Laboratories, Inc.

61. "Users Manual - Model 1600 FT-IR," Perkin Elmer, April 1989, Norwalk, Connecticut.

62. Virgil L.Anderson and Robert A. McLean, Design of Experiments, A Realistic Approach, Marcel Dekker, Inc., 1974, pp. 22.

63. Lyman Ott, An Introduction to Statistical Methods and Data Analysis, Third Edition, PWS-KENT Publishing Company, Boston, 1988, pp. 416.

64. Rupert G. Miller, Jr., Beyond ANOVA - Basics of Applied Statistics, John Wiley & Sons, 1986, pp. 89-92.

65. Mang Tia, Byron E. Ruth, Shin-Che Huang, Chui-Te Chiu, and Danny Richardson, "Development of Criteria for Durability of Modified Asphalts," State Project No. 99700-7529-119, UF Project No. 4910450431912, Department of Civil Engineering, University of Florida, Gainesville, 1994.

66. Raw data from the Material Office of Florida Department of Transportation, Mixing-Temperature Reduction Study offered by Mr. Kenneth H. Murphy, 1991.

BIOGRAPHICAL SHETCH

Chui-Te Chiu was born on May 15, 1962, in Taoyan, Taiwan, where he attended primary and secondary schools. He attended high school in Taipei, Taiwan, and received his high school diploma in June 1980. In June 1984, he received a Bachelor of Science degree in survey engineering from National Cheng Kong University, Tainan, Taiwan. After two years of military service, he worked for a construction company as a quality control engineer at the hot-mix asphalt plant. He attended graduate school at National Central University and started his graduate career in the field of civil engineering materials. He received his Master of Science degree in civil engineering in June 1989 and worked as a lecturer at Jang-Shing Junior College, Chung-Li, Taiwan. He came to the Department of Civil Engineering at the University of Florida for his Ph.D. study in January 1991.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Mang Tia

Mang Tia, Chairman
Professor of Civil Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Byron E. Ruth

Byron E. Ruth, Cochairman
Professor of Civil Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

David Bloomquist
Assistant Professor of Civil Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Andre I. Khuri
Professor of Statistics

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Gale C. Page
State Bituminous Materials Engineer
Florida Department of Transportation

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April, 1994

Winfred M. Phillips
Dean, College of Engineering

Karen A. Holbrook
Dean, Graduate School